U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

EXPLOSION AND FIRE

(3 Injured,* Potential Offsite Consequences)

FIRST CHEMICAL CORP.

PASCAGOULA , MISSISSIPPI

OCTOBER 13, 2002

KEY ISSUES

- EVALUATION OF REACTIVE HAZARDS
- APPLYING LESSONS LEARNED
- LAYERS OF PROTECTION
- WORK PRACTICES
- FACILITY SITING
- COMMUNITY NOTIFICATION

REPORT NO. 2003-01-I-MS

OCTOBER 2003

* One OSHA recordable injury and two first-aid injuries.

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Acronyms and Abbreviations

ACC	American Chemistry Council
ANSI	American National Standards Institute
API	American Petroleum Institute
ARC	Accelerating rate calorimeter
ASME	American Society of Mechanical Engineers
ºC	Degrees Celsius
CCPS	Center for Chemical Process Safety
CSB	U.S. Chemical Safety and Hazard Investigation Board
DBB	Double block and bleed
DCS	Distributed control system
DNT	Dinitrotoluene
EPA	U.S. Environmental Protection Agency
ESD	Emergency shutdown
ºF	Degrees Fahrenheit
FCC	First Chemical Corporation
HSE	Health and Safety Executive (United Kingdom)
IChemE	Institution of Chemical Engineers (United Kingdom)
IEC	International Electrotechnical Commission
ISA	Instrument Society of America
LEPC	Local emergency planning committee
meta-MNT	Meta-mononitrotoluene
mmHg	Millimeters mercury
MNT	Mononitrotoluene

MPC	Mississippi Phosphates Corporation
MSDS	Material safety data sheet
NFPA	National Fire Protection Association
NLL	Normal liquid level
ortho-MNT	Ortho-mononitrotoluene
OSHA	Occupational Safety and Health Administration
para-MNT	Para-mononitrotoluene
PHA	Process hazard analysis
PNMC	Para-nitrometacresol
psi	Pounds per square inch
psig	Pounds per square inch gage
PSM	Process safety management (OSHA)
PSV	Pressure safety valve
RMP	Risk management program (EPA)
RP	Recommended practice (API)
SIS	Safety interlock system
SOCMA	Society of Organic Chemical Manufacturers

Executive Summary

An October 13, 2002, explosion and fire at the First Chemical Corporation (FCC) facility in Pascagoula, Mississippi, had potentially catastrophic offsite consequences. The explosion propelled large fragments of debris offsite, several of which landed near crude oil storage tanks.

Steam leaking through manual valves heated mononitrotoluene (MNT) inside a distillation column and the material decomposed over several days, resulting in a runaway reaction and explosion. The column—which contained about 1,200 gallons of MNT, a potentially highly energetic reactive material when heated—was shut down at the time of the incident and thought to be isolated.

Debris from the explosion was propelled both onsite and offsite, resulting in a fire in an MNT storage tank that burned for almost 3 hours, and numerous smaller fires both onsite and offsite. Some of the debris landed in an adjacent facility near crude oil storage tanks, including one piece weighing over 6 tons. FCC emergency responders fought the onsite fires, while local community firefighters fought small fires along the public roadway. The Jackson County Emergency Management Agency called a shelter-in-place for the local community. FCC personnel began monitoring the air around the facility. Later that morning, the U.S. Environmental Protection Agency (EPA) arrived onsite and also monitored air quality.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) incident investigation revealed the following root causes:

- The FCC Pascagoula facility did not have an adequate management system for evaluating the hazards of processing MNT, and did not apply lessons learned from hazard analyses of similar processes in the plant.

- There was no system to ensure that the MNT column was equipped with sufficient layers of protection, including alarms, safety interlocks, and overpressure protection.

- The system for ensuring consistent work practices when isolating equipment was ineffective.

- The program to ensure the integrity of isolation valves in the steam line connected to the MNT column was inadequate.

CSB also determined that neither the construction nor the proximity of the control room to the process was evaluated to ensure that employees would be protected from catastrophic events. Likewise, the system for notifying the surrounding community about chemical releases or other hazardous incidents was inadequate to ensure that local residents were informed and knew what steps to take.

CSB makes recommendations to DuPont Chemical Corporation (which acquired the facility in November 2002); the Pascagoula facility; Jackson County, Mississippi; the American Chemistry Council (ACC); and the Synthetic Organic Chemical Manufacturers Association (SOCMA).

1.0 Introduction

1.1 Background

The October 13, 2002, explosion and fire at the First Chemical Corporation (FCC) facility in Pascagoula, Mississippi, resulted from the rupture of a 135-foot-tall distillation column (C-501)[1] that was used to refine mononitrotoluene (MNT). The column was thought to be isolated and in standby mode at the time of the explosion—approximately 5:25 am—though it contained a significant amount of MNT.

Debris from the explosion, including metal fragments and packing[2] from the column, was scattered throughout the facility and propelled offsite. One large fragment of the distillation column punctured a nearby para-MNT storage tank and ignited its contents, which burned for almost 3 hours. A 6-ton column segment was hurled 1,100 feet and landed near a crude oil storage tank at a refinery across the highway. Flying glass injured three FCC employees, who were in the unit control room at the time of the explosion. All three employees received first-aid, and one required additional medical treatment.

The FCC fire brigade fought the onsite fires, including the large para-MNT storage tank fire and numerous fires initiated by burning material on ejected column packing. Local community emergency responders provided backup and firefighting support for numerous small fires outside the facility. The sheriff's department provided traffic control. FCC personnel began monitoring the air around the facility. Later that morning, the U.S. Environmental Protection Agency (EPA) arrived at the scene and began air monitoring, and the U.S. Coast Guard conducted additional monitoring.

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[1] The #1 MNT still (C-501) was referred to as both the "still" and the "column." These terms are used interchangeably throughout this report

[2] Packing material was removable stainless-steel grating inside the column used to aid in the distillation process.

Because this incident had potentially significant offsite impacts and likely involved a reactive material, the U.S. Chemical Safety and Hazard Investigation Board (CSB) launched an investigation to determine the root and contributing causes, and to issue recommendations to help prevent similar occurrences.

1.2 Investigative Process

In conducting its independent investigation, CSB examined physical evidence, interviewed current and former FCC employees, and reviewed company documents and scientific literature. CSB investigators visited neighboring companies, including Chevron and Mississippi Phosphates Corporation (MPC), and surveyed the surrounding area in an effort to collect debris from the explosion. CSB contracted for testing of chemical samples and piping components, and also consulted with experts in the process and chemistry used at FCC. A community meeting was held on January 15, 2003, to gather information about the incident from local residents and interested parties.

1.3 First Chemical Pascagoula Facility

1.3.1 Facility Description

FCC is located on a 60-acre parcel east of Pascagoula, Mississippi, in the Bayou Cassotte Industrial Park. At the time of the incident, ChemFirst Inc., of Jackson, Mississippi—a member of the Synthetic Organic Chemical Manufacturers Association (SOCMA)—owned the facility. The plant employed 137 people and eight full-time contractors.

E. I. DuPont Nemours and Company was in the process of purchasing the FCC facility at the time of the incident and delayed the acquisition to review the consequent damage. DuPont officially acquired ChemFirst Inc. (the parent company of FCC) on November 6, 2002.

The facility is a major producer of aniline[3] and nitrotoluene intermediates and derivatives used in a variety of industries. It is one of the largest producers of aniline, and the world's second largest and only U.S. producer of nitrotoluenes.

Large bulk storage tanks for raw materials and finished products, warehouses and maintenance areas, control rooms and other office facilities, and the main office complex are located onsite. One building near the ruptured column housed the process area control room, locker room, offices, and a quality control laboratory (Figure 1).

Figure 1. Facility overview. (Note: The crane is attached to a column damaged in the explosion.)

[3] Aniline is an oily liquid from the aromatic amine family of chemicals, with the chemical formula $C_6H_5NH_2$.

1.3.2 Proximity to Other Industrial Complexes and Residences

The FCC facility is bordered by the following:

- To the south, Mississippi Phosphates Corporation (MPC), a fertilizer manufacturer—A large ammonia storage tank is located onsite; in addition, MPC also owns a large gypsum pile north of FCC.

- To the east, a Chevron refinery—Several crude oil storage tanks are located approximately 500 feet from the FCC property line. A highway and a rail spur are also located to the east of FCC.

- To the west, 0.25 mile, the Bayou Cassotte, a shipping route for businesses—A residential area is located to the west of the bayou.

1.4 Mononitrotoluene Process

1.4.1 Manufacturing and Refining of MNT

MNT is used in the production of dyes, rubber chemicals, and agricultural chemicals. It is an aromatic[4] nitro compound that is made by reacting toluene with nitrating acid, typically a combination of nitric and sulfuric acids. At the conclusion of the nitration reaction, the product—at this point consisting of MNT, residual acid, toluene, and water (a byproduct)—is sent to a separator, where the spent acid is concentrated and recycled back into the process. The rest of the product goes through a "washing" step and then flows to a toluene stripper to remove residual toluene. The resultant purified MNT liquid flows to a three-column distillation unit to separate the three isomers[5] of MNT—ortho-, meta-, and para- MNT.

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[4] An aromatic compound contains six carbon atoms that are interconnected, sometimes referred to as a "benzene ring."

[5] An isomer is two or more chemical compounds having the same atoms in the same proportion but differing in properties because of differences in molecular structure. There are three isomers of MNT.

1.4.2 #1 MNT Distillation Column

The vessel involved in the explosion, the #1 MNT distillation column (C-501), was the first of three distillation columns in the unit. It was 7 feet in diameter and approximately 135 feet tall.

During normal operation, the column runs under a vacuum to facilitate the separation process. Temperatures range from around 350 degrees Fahrenheit (°F) at the bottom of the column to near ambient at the top. Two steam-heated reboilers[6] supply heat. Eight temperature indicators are positioned throughout the column, though they are not equipped with alarms. A pump removes material from the bottom of the column (predominately para- and meta-MNT); the material is sent to a second distillation column for separation of the isomers, and it may also be circulated back to C-501. A reflux pump removes liquid (predominately ortho-MNT) from the top collector tray; the liquid flows through a cooler and is either sent to storage or returned to the top of the column. The column is filled with stainless-steel packing material to aid in the distillation process.

The facility central steam plant provides 300-pounds-per-square-inch-gage (psig) steam to the reboilers. The steam line to each reboiler is a 3-inch line with inlet and outlet manual block valves and a flow control valve in series. A bypass line around the control valve contains a manual block valve.

[6] A reboiler for a distillation column is a heat exchanger that generally has process material flowing through one side and a heating medium, such as steam, flowing through the other side. When steam is used, it heats the process material—which, in turn, warms the material in the bottom of the vessel, causing the components with lower boiling points to vaporize.

2.0 Description of Incident

2.1 Pre-Incident Events

Five weeks before the incident, on September 5, 2002, the Pascagoula FCC facility experienced problems with the sulfuric acid concentrator upstream of the MNT unit. FCC decided to shut off the feed to the MNT distillation columns, including the #1 MNT column (C-501), on September 7 (Table 1). C-501 contained approximately 1,200 gallons of MNT at the time; the column was left on total reflux.[7] Due to low product demand, the decision was made not to start up the columns in the MNT unit until work associated with the plant-wide shutdown (scheduled for early October) was completed.

Table 1

Condensed Event Timeline, September 7–October 13, 2002

Date (2002)	Event
Sept 7	Feed to distillation column shut down; column left on total reflux
Sept 22	Fire in the hydrogen unit; steam isolation valves closed
Sept 27	Vacuum broken on distillation column
Sept 29	Entire facility shut down for maintenance turnaround
Oct 5	Plant boilers brought back online
Oct 5-13	Temperature steadily increases at column bottom
Oct 13	Distillation column wall breached, seconds later column ruptures at 5:25 am

[7] "Total reflux" means that steam continued to be fed to the reboilers, but no fresh feed flowed to the column. Although material was continuously recycled through the column, no product was removed and sent to storage.

On September 22, a fire occurred in the # 2 hydrogen unit, which could have affected steam production for the facility. Operators quickly attempted to isolate the heat sources to columns that were not considered priority at the time, such as columns on reflux (including C-501). For both steam stations, operators closed the manual valve to the reboilers, downstream of the control valve (shown as valve "2" in Figure 2). The manual valve in the bypass line (valve "1" in Figure 2) was normally left in the closed position. The distributed control system[8] (DCS) sent a signal to the control valve to close (valve "3" in Figure 2).

For the next 5 days, the valves on the steam line remained closed; however, DCS information reviewed after the incident indicates that the temperature in the base of the column did not fall below 300°F. The temperature would have been expected to decrease to around ambient if no heat was being added.

In early September, the Pascagoula plant was completing preparations for the annual plant turnaround, scheduled to start on September 29. Approximately 1,200 gallons of MNT was left inventoried in C-501, and the manual valves remained closed. There was no followup audit of the isolation of the column going into the longer term shutdown.

On September 27, in preparation for maintenance on the reflux cooler, unit operators "broke" the vacuum in C-501 (i.e., pressurized the column) by injecting nitrogen into the system. Nitrogen feed was provided through a tubing connection to the top head vapor discharge line. Because the pressure gauge measured only the degree of vacuum on the column and had a range of 0 to 200 millimeters mercury (mmHg), there were no data to verify that the vacuum was fully broken.[9] According to DCS data reviewed after the incident, the temperature in the bottom of the column continued to rise to approximately 415°F.

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[8] A distributed control system is an automated system used to control and monitor a chemical process.

[9] Failure to fully break the vacuum in the column likely led to air being introduced, which was not subsequently purged. The presence of air can increase the reaction rate of MNT, as discussed in Section 3.0.

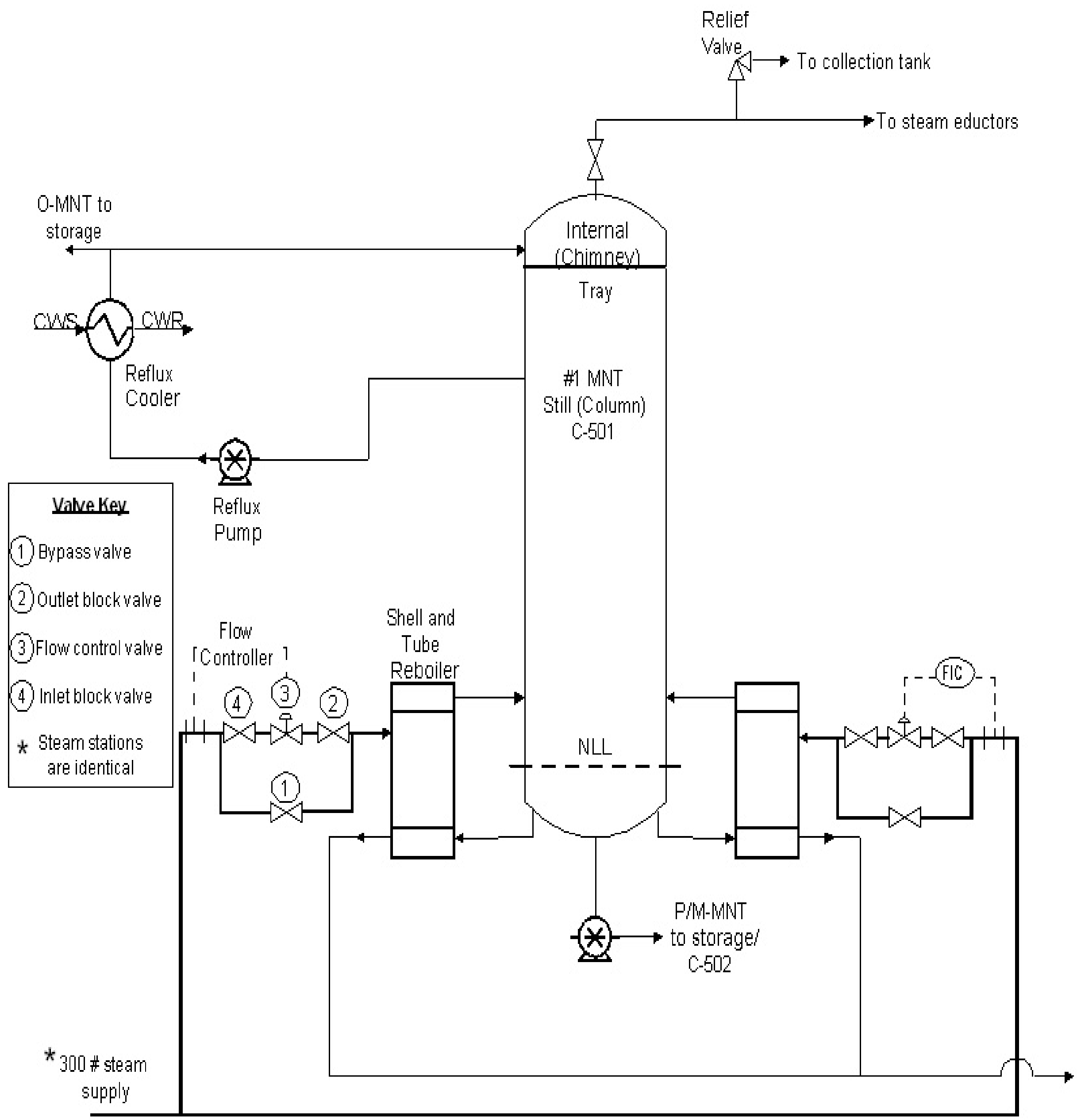

Figure 2. #1 MNT distillation column (C-501) and related equipment.

Operations personnel did not actively monitor the temperature. Figure 3 shows a chart of the DCS data for the bottom two temperature indicators.

On September 29, the plant steam boilers were shut down for scheduled maintenance. The temperature in C-501 cooled to near ambient. Power was lost to DCS on October 1 and restored the next day; the hard drive on the control system was lost on October 3 and restored the following day. No DCS data are available for these times.

Maintenance on the boilers was completed on October 5, and the system was brought back online. The temperature of the material in the bottom of the column increased to approximately 415°F by mid-morning.

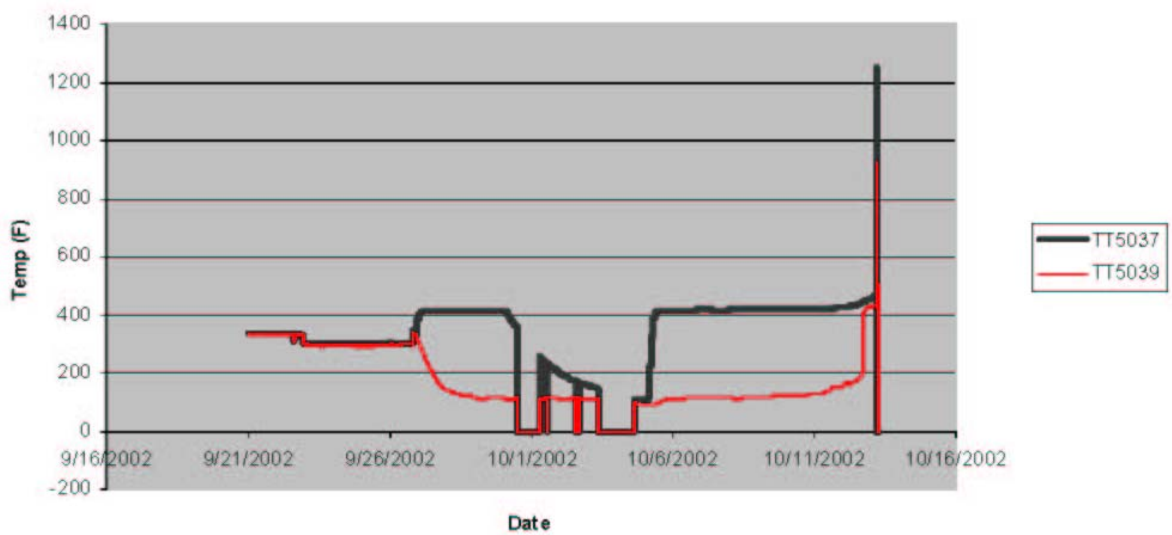

Figure 3. Temperature at column bottoms, September 21–October 13, 2002.
(Note: Thermocouple TT-5037 [the top line shown for 10/11/2002] was at the bottom of the vessel, and TT-5039 was above the reboiler inlet line.)

2.2 Incident Description

2.2.1 Day of Incident

The temperature of the material in C-501 continued to rise following the boiler startup on October 5, until it reached over 450°F on the morning of October 13. There is no evidence that the temperature was being monitored by operations.[10] The higher temperature at the base of the column likely vaporized some material, which was carried up the column and accumulated on the "chimney tray" at the top. On the morning of October 12, a high level alarm for the tray actuated; it was silenced by the operator, but no further action was taken.

Early on October 13, an operator in the area of C-501 heard a rumbling sound, which was followed by an increasingly loud sound described as being similar to a relief valve venting.[11] Operators in the area noticed material venting at a high velocity from an apparent horizontal breech in the upper half of the column; it was described as smoke or steam or "snow." One eyewitness described the material as "blowing to the east," toward Chevron. One operator left the control room to investigate and quickly determined that the only safe action was to return. He instructed two other operators to stay inside the control room, which was located only about 50 feet from the base of the column.

According to eyewitness testimony, a few seconds to minutes later, the column ruptured and an explosion occurred. The force of the explosion knocked down the three operators who were standing just inside the control room door; they received cuts and abrasions from shattering glass. One operator said he saw a fireball move past the door.

The force of the explosion propelled the top 35 feet of C-501—both the vessel head and approximately 30 feet of the cylindrical shell—offsite. All the structured packing inside the column was ejected, and burning residue on the packing material inside the column was also blown out and offsite. A large column sidewall fragment hit a storage tank approximately 500 feet away, which held more than 2 million pounds of para-MNT, resulting in a fire in and around the vessel. The cooling tower for the unit was also struck by debris and caught fire.

[10] No alarms were associated with the temperature indicators.

[11] CSB examined the relief valve and downstream tank after the incident and determined that the valve did not open during the event.

The pressure of the explosion damaged a number of buildings onsite, including the control room. Almost all of the acoustical drop ceilings in the control room and adjacent laboratories and breakrooms collapsed. The roof was extensively damaged, cinderblock walls were cracked and distorted, and the exterior doors were buckled and glass broken. An administration building—located over 400 feet from C-501—was also significantly damaged, including impact from a piece of shrapnel that punctured the cinderblock wall adjacent to an office. A number of additional steel-frame construction buildings sustained damage to roll-up doors and corrugated siding on the side facing the failed column.

2.2.2 Area of Impact and Potential Consequences

The explosion propelled large fragments from the vicinity of the column. A piece of shrapnel struck a pipe rack directly above a 500,000-pound anhydrous ammonia tank onsite. A 6-ton piece of column sidewall was hurled onto Chevron property, approximately 1,100 feet away; it landed an estimated 50 feet from a 250,000-barrel crude oil storage tank. A valve and portions of piping were also found on Chevron property as much as 1,700 feet from the column.

Within this radius of potential impact were several pieces of equipment that contained flammable and toxic material, including tanks and piping. As previously discussed, a crude MNT storage tank at FCC (which contained para-MNT) was hit by shrapnel and caught fire. A number of other potential receptors, including chlorine cylinders and sulfuric acid tanks, were located within the area of debris. If debris had hit this equipment, it is likely that the incident would have caused significant secondary releases of material. (See Figure 4 for an aerial map of FCC and the surrounding area.)

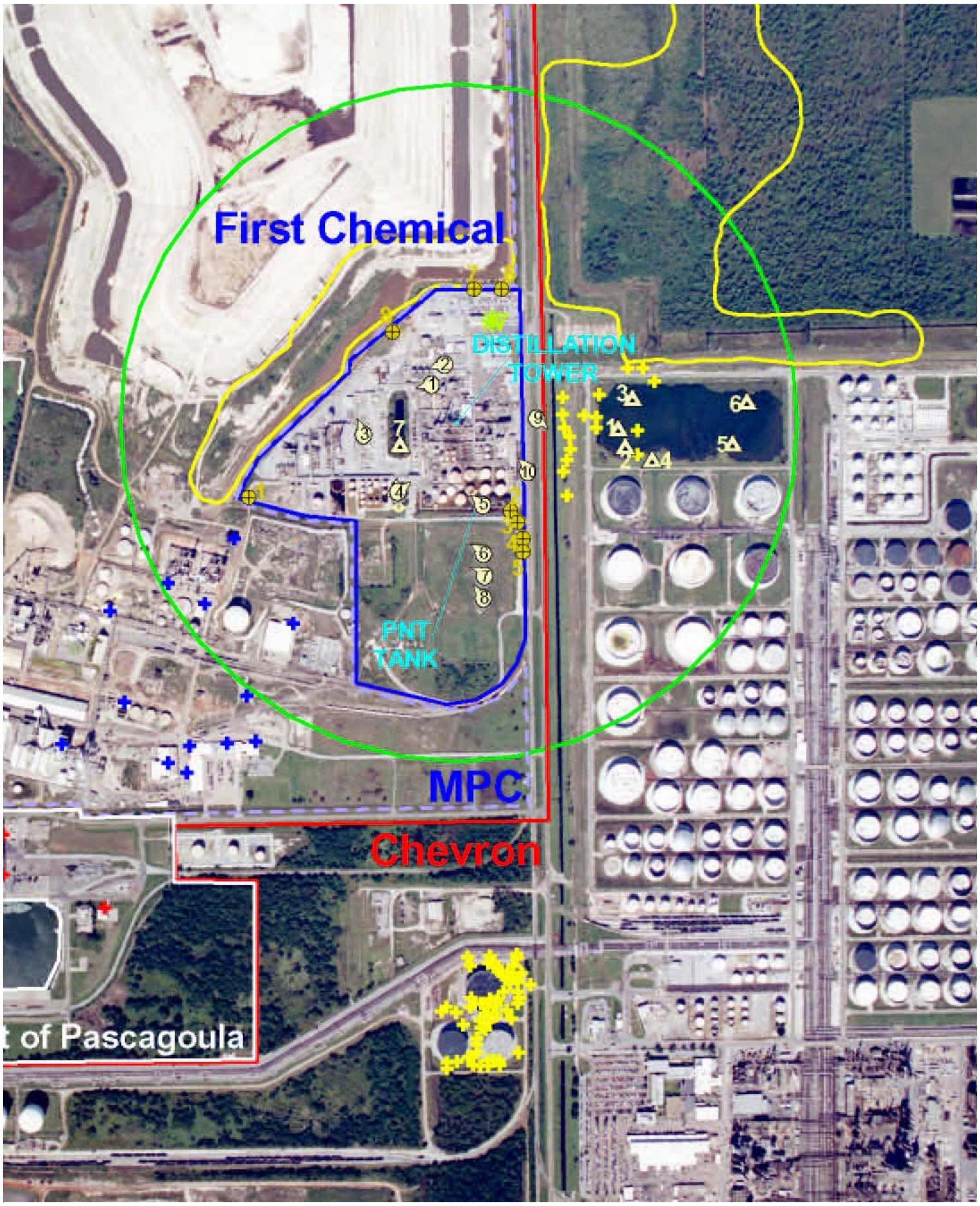

Figure 4. Aerial map of FCC facility showing post-incident debris pattern.
(Circle shows a 2,000-foot radius from the column, where the search for debris occurred; numbered triangles show the location of various metal debris; crosses denote areas where some of the packing landed outside FCC property.)

2.2.3 Emergency Response

Following the explosion, the operators gathered and accounted for each employee. They then used water monitors and other firefighting equipment to put out the small fires caused by burning debris. Local firefighters extinguished fires along the public highway.

Wind blew the black smoke from the facility in an eastwardly and southeasterly direction over Chevron property and the Gulf of Mexico. The Jackson County Emergency Management Agency called a shelter-in-place[12] for nearby residents, and a no-fly zone was established for 1 mile around the facility. The largest fire was in the para-MNT storage tank. All fires were extinguished by 8:30 am on October 13.

2.3 Reconstructive Analysis

To assist in determining the causes of the explosion in the #1 MNT column (C-501), the CSB investigation team analyzed various aspects of the explosion and factors leading up to it. CSB commissioned a geographic grid search for pieces of the vessel, and also conducted testing of the steam control stations, chemical samples, and metallurgy samples.

2.3.1 Grid Search

FCC contracted out the initial search for explosion debris. The contractor found light fragments (e.g., aluminum packing and strapping) mainly to the south and east, up to 0.7 mile from the facility; a portion of this material landed on a Chevron storage tank due south of the column.

Heavy fragments were concentrated mainly in a large storage tank farm to the east, also on Chevron property. The largest piece of debris was a section of the top of the column, which weighed

[12] A shelter-in-place is called to minimize potential exposure to chemicals. The steps include going inside a secure enclosure such as a house, closing all windows and doors, turning off ventilating equipment to prevent chemical ingress, and monitoring local television or radio stations for further instructions.

approximately 13,500 pounds. It was found about 1,100 feet from the base of C-501. The 7-foot-diameter head of the column was not found during these searches. In November, FCC again used the contractor for a search of two cooling water ponds located on Chevron property. Magnetometers were used; the head of the column was not found, though several other large pieces were recovered. Among the items were a large section of grating, a 4-foot-long section of 1-inch piping, and two valves—one weighing 50 to 60 pounds. The large valve was estimated to have traveled 1,425 feet from the column.

In an effort to locate additional physical evidence, including the head of the column, CSB investigators conducted a search of a used equipment area on MPC property in December. CSB also commissioned a contractor to search areas not covered previously within a 2,000-foot radius of the column. The entire search area covered over 81 acres.[13]

2.3.2 Steam Control Stations

CSB examined how heat could have been applied to the MNT that remained in C-501 after it was shut down. Separate supply lines carried steam to the two reboilers at the base of the column. Manual valves downstream of the control valves in both lines and both bypass lines were closed on September 22, as confirmed by log entries, interviews, and the as-found position of the valves. In addition, the flow control valves had been commanded closed from DCS. CSB tested both valve stations to determine if they had leaked and the likely cause. Each station consisted of four valves, as shown in Figure 5.

[13] The column head and other associated debris were never located.

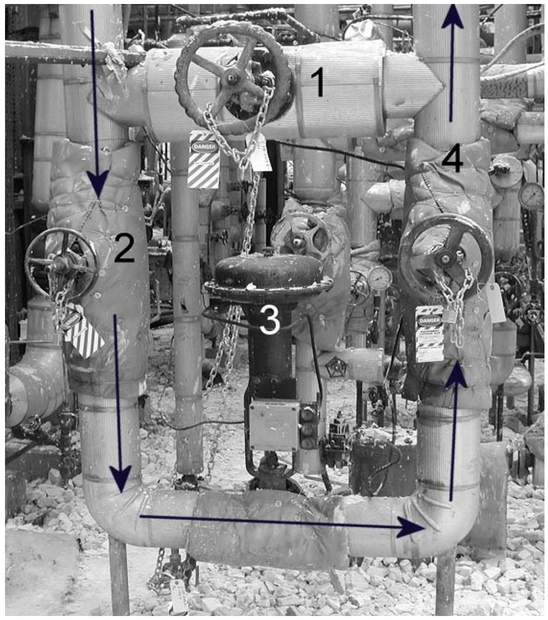

Figure 5. Steam line to reboiler. (The numbered valves represent: (1) manual valve in the bypass line, (2) inlet block valve, (3) automatic flow control valve, and (4) outlet block valve.)

CSB contracted to have the steam stations tested in the as-found condition of the valves to determine leak rate. Data from these tests showed that the manual valve in the bypass line for one of the stations was leaking significantly, over 180 pounds/hour. Corrosion and erosion caused a breach in the valve; the steam flow caused holes to form in the seat of the valve, one of which is shown in Figure 6.

Examination of the other steam station indicated that it leaked as well. Although the manual valve in the bypass line (i.e., valve "1" in Figures 2 and 5) did not appear to leak, the facing on the outlet block valve (the valve downstream of the flow control valve) was severely scored from corrosion products and debris in the system. Because the flow control valve was not intended to be a tight shut-off valve, steam likely leaked through the main branch. Based on examination of the outlet-blocking valve for that station (i.e., valve "2" in Figures 2 and 5), it is believed that debris and particulates may have prevented the valve

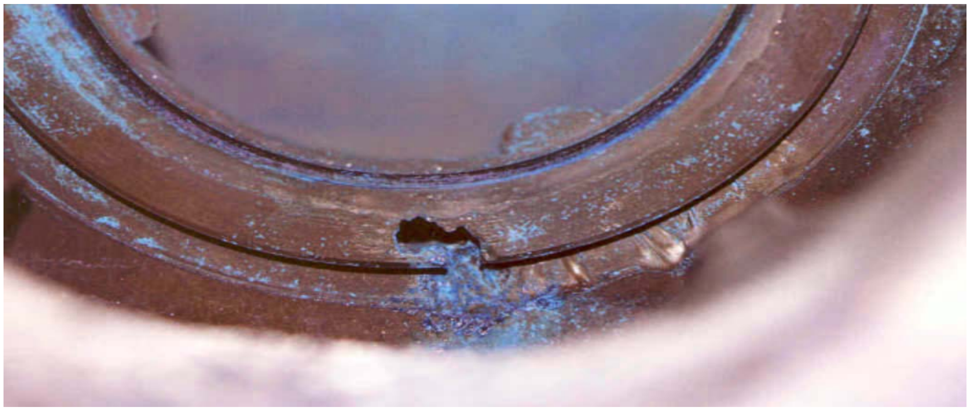

Figure 6. Breach in valve seat for bypass valve.

from seating properly. The steam system was “moist”—meaning that it contained liquid as well as steam vapor, which contributed to additional erosion and corrosion of the piping system.

These results verify that steam likely leaked through manual valves and continued to heat material in C-501, even though the valves were in the closed position. These findings are consistent with DCS data, which indicate that there was flow through the line when the valves were closed and believed to be isolating the steam source from the MNT column (Figure 7). DCS data, though exhibiting an erratic pattern, indicate even higher flow rates than were found during CSB testing. Although the registered flow rates indicated in the DCS data may not be correct, they illustrate that flow was occurring in the system at a time when the column was believed to be isolated.

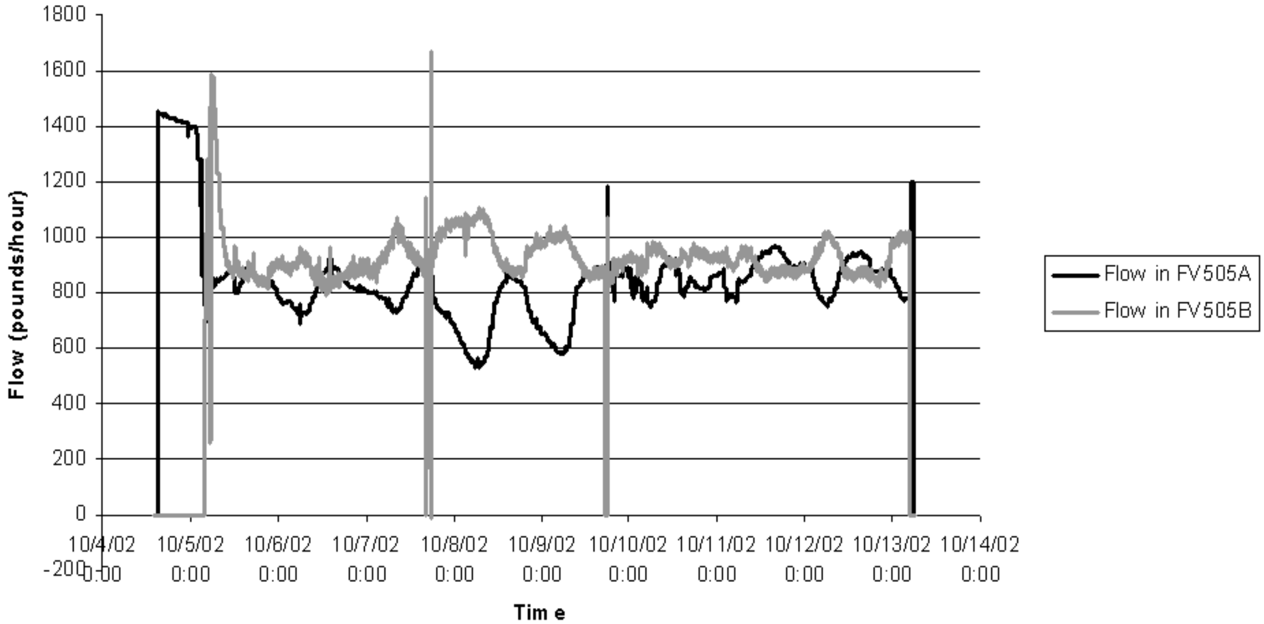

Figure 7. DCS readout of steam flow to reboiler when system was believed to be isolated.

2.3.3 Thermal Stability Testing

The chemistry of nitrotoluenes has been studied for a number of years. Nitrotoluenes may decompose when exposed to high temperatures instantly or elevated temperatures for an extended time. The decomposition mechanism generates gases, which can build pressure if the material is confined. C-501 was shut down with 1,200 gallons of material in the base and exposed to a heat source for an extended time. CSB investigators theorized that the explosion occurred due to a thermal decomposition of MNT.

To verify this theory, CSB arranged for testing of fresh MNT samples collected upstream of C-501. (Because of the incident, there was no material to sample in the column itself.) The feedstock samples contained all three isomers of MNT. They were representative of the MNT that would be expected to be in the column, except that they contained approximately 3 percent toluene, which would have been removed from the feedstock by the toluene stripper prior to entering C-501. Because of the low amount of toluene present, the samples were tested as received. No other contaminants were found in the samples.

Adiabatic calorimetry testing was conducted on the samples.[14] The initial test used the heat-wait-search method, in which the sample temperature was increased until reaching an exotherm, after which the sample was allowed to self-heat under adiabatic conditions. This initial test was used to determine the temperature at which decomposition begins. The MNT sample showed an exotherm beginning at 273 degrees Celsius (ºC [523°F]), with maximum rates of temperature and pressure rise of 1,500°C/min and 100 bar/min.

The adiabatic calorimeter was also used to perform induction time[15] measurements between 240° and 265°C (464° and 509°F). The values were extrapolated to estimate the induction times under conditions similar to those at FCC.

Between 415° and 454°F—roughly the temperature range of MNT column bottoms during several days prior to the explosion—the induction time for self-heating would have decreased from about 35 days (at 415°F) to just over 1 day (at 454°F), as shown in Figure 8. The column bottoms temperature was measured at 454°F a few hours before the explosion. Thus, the induction data are consistent with a self-heating reaction.

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[14] Adiabatic calorimetry is a chemical testing technique that determines the self-heating rate and pressure data of a chemical under near-adiabatic conditions. (Adiabatic refers to any change in which there is no gain or loss of heat to the environment.) This measurement technique estimates the conditions for, and consequences of, a runaway chemical reaction.

[15] Induction time is the amount of time that a material must be held at a certain temperature before an exotherm (in this case, a decomposition) is observed. Materials may decompose if they are exposed to their "onset" temperature (lowest temperature at which decomposition activity is observed), or if they are held at an elevated (but lower) temperature for an extended time.

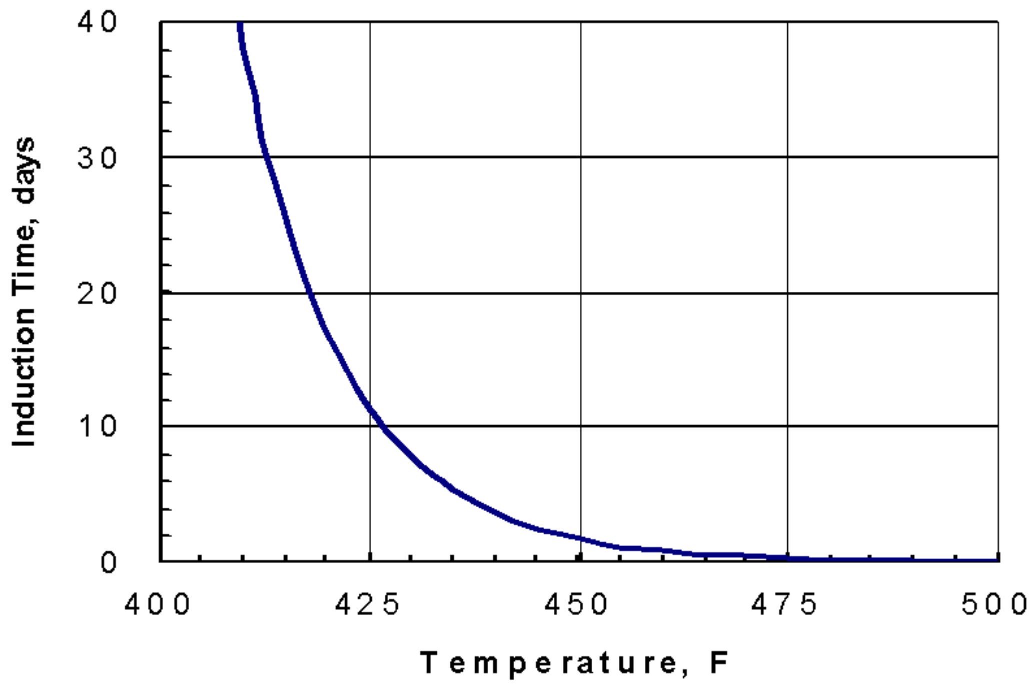

Figure 8. Mononitrotoluene induction time-temperature data on linear scales.

These results are consistent with information found in literature concerning the decomposition of MNT. In a paper presented at an Institution of Chemical Engineers (IChemE) symposium, the authors note that a number of incidents occurred when MNT was heated to excessively high temperatures or held at more moderate temperatures for an extended time (Harris, Harrison, and MacDermott, 1981). The latter phenomenon is referred to as the “induction effect.” For large batches of material (on the order of the amount in C-501 prior to the incident) that are exposed to temperatures between 401° and 419°F, a violent decomposition will occur within 8 to 25 days. This is consistent with conditions at FCC prior to the incident.

In a *Journal of Loss Prevention Process Industries* article, Chen and Chai-Wei (1996) note that the decomposition of MNT occurs in two phases. Phase one is a slower self-heating initiated at 284°F, and phase two is an accelerated self-heating initiated at 392°F.

As part of its investigation of the incident, DuPont also considered the possibility of an additional decomposition that involved material on an internal tray toward the top of the column. The material was thought to be mostly ortho-MNT because it had a lower boiling temperature and was the isomer most likely to accumulate in the upper part of the vessel. According to DCS data, the tray lost its contents within a matter of seconds just before the explosion. DuPont attributed this loss to the tray being damaged by a pressure impulse due to decomposition in the base of the column. The (predominantly) ortho-MNT contacted fouling residue when it spilled onto the packing below. DuPont conducted testing on the solids in the residue—which contained enamine, azo, and azoxy groups—and determined that they significantly lowered the onset decomposition temperature. The presence of air in the column, as well as pressure, was also determined to make the material more reactive.

DuPont determined that the following factors contributed to a secondary decomposition in the top part of C-501:

- The MNT on the top tray was the more reactive ortho-MNT.
- The presence of solids on the packing lowered the onset temperature of decomposition.
- Air was introduced into the column during maintenance work.
- The column was kept under pressure rather than being kept under vacuum after maintenance.

CSB reviewed the results of the DuPont investigation. Additional evidence in literature suggests that the factors present could have caused a more energetic reaction. In his book *Distillation Operation*, Kister (1990) notes a previous incident in which MNT was held at 150°F and air was introduced. A previously unknown exotherm set in, causing an explosion. Duh et al (1997) note that ortho-MNT is more unstable than the other isomers, as represented by a lower onset temperature and a higher heat of reaction. Although it cannot be stated conclusively that a secondary explosion occurred in the top of the column, it does present a plausible explanation for the burst of energy that separated the vessel. (See the causal factors diagram in Appendix A.)

2.3.4 Vessel Integrity Testing

To determine if thinning of the column wall could have been a causal factor in the incident, CSB investigators examined the upper portions of C-501 and found that the metal had thinned to only 30 percent of its original thickness—most likely due to external corrosion under the insulation. This finding raised the possibility that vessel integrity was a factor in the incident. The design drawing[16] and nameplate for C-501 show the design pressure as 15 pounds per square inch (psi).[17] When thermal stability testing was performed, the pressure in the test chamber reached approximately 240 psi before the testing equipment shut down, indicating that the pressure in the vessel likely exceeded this value.

The thermal stability testing contractor calculated that the ultimate pressure generated inside the distillation column due to decomposition could have been as high as 3,800 psi. Even if the vessel wall was not thinned, the column could not have withstood this pressure. CSB concluded that the vessel would have eventually ruptured even if there had been no degradation of wall thickness.

[16] MNT Tower (AS-501) Aniline Plant, First Chemical Corp., Pascagoula, Mississippi, Dwg. No. E1552-305A.

[17] It is important to note that the design pressure for vessels generally includes a safety factor. A vessel is expected to withstand a somewhat higher pressure than design before failing.

3.0 Analysis of Incident

Among the factors contributing to the incident at FCC are the following:

- Inadequate understanding of the potential hazard of thermal decomposition in continuous processing equipment.
- Insufficient instrumentation to allow monitoring and control of the process to prevent a catastrophic release.
- Lack of a system to ensure isolation of heat sources.
- Inadequate preventive maintenance, which allowed leaks in isolation valves.

The consequences of this incident were also exacerbated by inadequate evaluation of the location and structure of the control room, and poor community notification.

3.1 Reactive Chemical Hazard Management

3.1.1 Background on Mononitrotoluenes

The distillation column involved in the October 13 incident (C-501) separated three different isomers of MNT. Bretherick (1999) notes that explosions have occurred during fractional distillation to separate mixed nitrotoluene isomers when they were excessively heated or when materials were held at more moderate temperatures for an extended time. MNT may decompose explosively if heated above 190°C (374°F; Lewis, 1996).

3.1.2 Hazard Evaluations for Batch Distillation Project

The isomers of MNT can be separated by either batch or continuous distillation. The #1 MNT column (C-501) was part of a continuous process (i.e., MNT feedstock was continuously sent to it, and it was continually heated to separate the lower boiling material from the other isomers). FCC personnel considered MNT to be stable when it was separated in the continuously operating stills. They could not recall any previous incidents in which the temperature or pressure had increased rapidly in the MNT stills.

In 1996, the Pascagoula facility decided to perform additional MNT isomer separation using a column that was already onsite. The separation took place using batch technology, where a specific volume of material is pumped into the column in "batches" and then heated to the desired temperature until the appropriate amount of ortho-MNT is distilled. This batch distillation process involved a larger inventory of material than the continuous process and had not been performed previously at the site.

In contrast to the continuous stills—for which no process hazard analysis (PHA) was conducted prior to the incident—FCC performed a PHA of the equipment in the batch process in March 1996. The PHA included literature searches on the thermal stability of MNT as well as data from previous incidents involving the material. As a result of this effort, operating limits were added to the procedures, and recommendations were developed and implemented that resulted in additional safeguards being added to the batch vessel.

According to at least one data source documented in e-mails and interoffice memoranda, a safe distillation temperature was no more than 374°F (190°C). It was noted that this value agreed with accelerated rate calorimeter (ARC)[18] work performed on behalf of FCC, where an onset of an exotherm[19] was detected around 365°F for the material that would be charged to the batch still. The safe conditions under which to

[18] ARC is a measurement technique designed to provide temperature–time and pressure–time data of chemical decompositions.

[19] An exothermic reaction is characterized by the release of energy.

operate the still were set at "<370°F," with a high temperature alarm at 400°F, and it was noted that "the potential for an exotherm is always present, but if the heat is continuously removed from the material . . . self-heating is not allowed to propagate."

FCC commissioned two laboratories to conduct further thermal stability testing. In a memorandum summarizing those results, it was noted that nitrotoluene isomers are not expected to become thermally unstable unless heated past 250°C (482°F); and at an operating temperature of 370°F, there would be a "safety margin of over 100°F." However, one of the laboratories presented the following caution in its report:

> . . . Lengthy exposure to high temperature, *even below the exotherm detection point*, can influence the behavior. These chemicals may therefore undergo decomposition *at lower temperatures than those found in this study* depending on their previous exposure history." (Italics added for emphasis.)

3.1.3 Instrumentation for Batch Process

In April 1996, a list was developed to ensure that the PHA recommendations were addressed prior to startup of the batch distillation. One of the recommendations was the addition of an interlock to stop the flow of the heating medium (i.e., hot oil) to the reboiler if the temperature in the column was too high. The column also contained an interlock that stopped hot oil flow to the reboiler if the pressure in the vessel was too high (i.e., represented by a loss of vacuum).

3.1.4 Procedures for Batch Process

The procedure put in place to perform distillation on the batch column (AS-310) contained notes under a section called "Safety Items." One of the notes stated: "Any time the still pot bottoms temperature exceeds 400 degrees F shut down the hot oil flow and closely monitor the bottoms temperature." A second note cautioned operations personnel not to allow the temperature in the still pot to exceed 395ºF for more than 1 hour due to "product breakdown." Another note cautioned operators not to "allow the heat to stay on the still pot if the desired vacuum is not available!"

3.1.5 Good Management Practices

Managing chemical reactivity is a core competency of the chemical industry. The Center for Chemical Process Safety recently published *Essential Practices for Managing Chemical Reactivity Hazards* (CCPS, 2003). Although the design and operation of the MNT batch and continuous units at FCC predate this publication, many of the steps taken in conjunction with the batch distillation of MNT were consistent with CCPS guidance.

Steps recommended by CCPS include collecting, identifying, and testing for chemical reactivity hazards; assessing reactivity risks; identifying controls and management options; and reviewing and auditing the program. The FCC literature search focused on thermal stability; additional testing to confirm stability; conducting a PHA to evaluate risks; addressing recommendations, including adding interlocks to stop heat input based on high temperature; and having explicit warnings in operating procedures—all critical items in an effective program.

The actions taken in conjunction with the batch distillation project demonstrate the degree of diligence in place when the process was developed. However, there was no system to apply evaluation results from the batch process to continuous processing equipment. No hazard analysis system was in place for the continuous MNT distillation columns because—in this older, ongoing production process—the potential hazards were not fully recognized or properly managed.

At the time of the incident, there was no high temperature interlock in place to shut off the heat source to the continuous MNT column (C-501), similar to the one that had previously been added to the AS-310 column. Also, the operating procedures for C-501 did not emphasize the cautions that were listed in the AS-310 procedures.

The batch column processed a higher volume of material than C-501. Furthermore, C-501 had a successful operating history. Because of these factors, FCC took a different approach in the hazard evaluations of the two processes and did not do a formal hazard evaluation of C-501. However, the operating practices associated with C-501—including leaving material in the column when the unit was shut down and not verifying positive isolation of the heat source—made the conditions in the vessel at the time of the incident similar to those in the batch column.

3.1.6 Applying Lessons Learned

CCPS (2003) notes that:

> Multiple facilities in an organization may have similar chemical reactivity hazards . . . or use similar technology to control the associated hazards. If so, it may be more efficient for a corporate office or personnel to assume responsibility for some improvement activities . . . This can also facilitate communication of incidents and best practices between facilities.

Although this comment is aimed at sharing best practices among different facilities, it also applies to different units or processes at the same facility.

The MNT continuous unit processed the same material as the batch unit. If FCC had a program in place to proactively identify hazards in the continuous unit, or broadly applied knowledge acquired during hazard review of the batch unit, it is likely that additional hardware and administrative safeguards would have been implemented. This proactive approach of conducting evaluations when new information is acquired is preferable to conducting them only when existing equipment or procedures are changed.

3.2 Monitoring and Instrumentation

The #1 MNT column (C-501) processed material that could undergo decomposition. An important aspect of safely processing such material is to have appropriate instrumentation in the form of indicators, alarms, and active controls. Indicators and alarms warn operators of upsets. As another layer of protection, active controls—such as safety interlocks and emergency shutdown (ESD) systems—use the output from indicators to automatically correct problems. This instrumentation should be functional at all times, even when equipment is in abnormal operating conditions, such as extended shutdown.

In *Guidelines for Engineering Design for Process Safety,* CCPS (1993a) notes that the concept of layers of protection applies to the design of control systems: "Facilities which process hazardous materials should be designed with multiple safety layers of protection." CCPS reiterates that multiple layers addressing the same event are often necessary to achieve high levels of certainty that protection will be available when needed. Automatic action safety interlock systems (SIS) or ESD systems provide a layer of protection if primary barriers to failure—such as critical alarms, operator supervision, and manual intervention—do not correct a deviation. In some processes, it may be necessary to have a quench system to remove heat if the temperature rapidly increases. The interlock installed on the batch MNT distillation column (A-310) in 1996 to stop hot oil flow to the reboiler in the event of high temperature is an example of an active control (Section 3.1).

As discussed previously, FCC did not evaluate or fully understand the potential hazards of handling MNT throughout the continuous process, as reflected in the lack of instrumentation on C-501. Six temperature indicators, positioned from the bottom to the top of the column, were functioning at the time of the incident. The indicators sent a DCS signal to the operator's computer screens. However, unlike the batch distillation process, there were no alarms on the indicators—and there were no interlocks on the column, which would stop the heat input to the column if the temperature was too high.

Essential Practices for Managing Chemical Reactivity Hazards emphasizes that the basic process control system and protective safeguards must be designed, operated, and maintained to a high standard (CCPS, 2003). Analysis techniques to evaluate both the basic process control system and SIS are not only an issue in new construction, but also throughout active operation (CCPS, 1993).

ANSI/ISA-84.01[20] notes that the following steps are necessary to determine the appropriate safety system level for instrumentation (including sensors, alarms, and shutdowns):

- Conduct a PHA
- Assess risks
- Apply protective layers
- Determine if further safeguards are required.

ANSI/ISA-84.01 provides no specific guidance on these steps, noting that each company selects preferred tools for risk evaluation.

When the batch column was brought online in 1996, FCC conducted a PHA and determined that an additional interlock was necessary to stop the flow of heating medium to the reboiler if the temperature in the vessel was too high. There was no evidence that a PHA was performed on C-501 or that consideration was given to the appropriate level of instrumentation. The last line of defense in protecting a column is often the relief device (Section 3.5).

[20] This joint publication by the American National Standards Institute (ANSI) and the Instrument Society of America (ISA), *Application of Safety Instrumented Systems for the Process Industries,* provides guidelines on how to design, operate, and maintain safety-instrumented systems, such as high-temperature interlocks. Other industry standards include those of the International Electrotechnical Commission (IEC, 2003).

Having an evaluation system to determine the necessary level of instrumentation and control, similar to the one outlined in ANSI/ISP-84.01, would have provided FCC with the opportunity to review its instrumentation for process monitoring and process control. Such a review would have helped to ensure that critical equipment was consistently instrumented throughout the facility and may have led to the addition of safeguards on C-501, which would have decreased the likelihood of the October 13 incident.

3.3 Safe Work Practices

Effective training, standardized procedures for safe practices, and communication are essential to ensure that work practices are complete and consistent throughout a facility. As discussed in Section 3.1, FCC did not evaluate or fully understand the potential hazards of handling MNT throughout the continuous process, which was further demonstrated by the lack of an effective system to ensure safe work practices.

Effective operating procedures should:

- Address all modes of operation, including abnormal situations such as extended shutdowns for all foreseeable causes and startup after shutdown.
- Specify the critical parameters to monitor (such as temperature), even when the column is shut down.
- Provide information about the hazards of materials being processed, operating limits, and actions to take if limits are exceeded.
- Specify how to accomplish critical tasks such as isolation.

The FCC procedure that guided operation of C-501 was entitled "#1 MNT Still/#2 MNT Still and Toluene Stripper."[21] It did not provide any cautions about the nature of MNT, potential instabilities of the material, or safe operating limits and the consequences of deviations. In contrast, the operating procedure for the MNT batch process[22] included cautions and required operators to shut down the heat source if the temperature exceeded 400°F. The procedure for the batch process also included actions to take in the event of self-heating.

The procedural section on emergency shutdown instructed operators on how to shut down C-501 in the event of steam failure (presumably to the overhead eductors) or cooling water failure. No other situations—such as isolating the column to allow operators to assist in another unit, as happened on September 22—were discussed. In the case of steam failure, the instruction directed operators to "place the steam to the reboiler control valves in manual and closed position," and "block in condensate return off each reboiler."

The flow valves were not designed to be tight shutoff valves. The instructions did not specify that the steam line to the reboilers should be double-blocked-and-bled (DBB),[23] even though operations personnel noted that they knew those were the steps necessary to isolate the line. In addition, the practice at the time of the incident did not include placing blinds in the steam line, which would have provided an additional degree of isolation.

Although the normal practice was to leave material in the column during shutdown (unless it was to be entered for maintenance), the procedures did not provide any guidance on monitoring conditions in the column (including temperature) while it was shut down. From October 5—when the boiler was

[21] *#1 MNT Still/ #2 MNT Still and Toluene Stripper*, Document No. 1201.003-1003, Revision 11, FCC.

[22] *AS-310 MNT Distillation*, Document No. 1201.003-1702, Revision 6, FCC.

[23] Double-block and bleed (DBB) and blinding are two methods of isolating material. For DBB, two valves are closed and a drain is opened between them so that any accumulated material flows through the drain and not through the valve. A "blind" is a solid plate installed in piping to prevent material flow.

restarted—until the day of the incident, the temperature steadily rose and was well in excess of the 400°F limit specified in the batch distillation procedure.

Along with procedures, communication about current conditions and training are vital to the safe and efficient operation of a process facility. Effective training teaches employees how to safely perform their jobs under normal and abnormal situations. CCPS (2003) notes that communication and training cannot be overlooked when developing programs to control chemical reactivity hazards: "All operating personnel should have a good idea of what will happen if . . . a process is operated in the wrong range." Although level accumulation on the top tray of C-501 was not the cause of the decomposition reaction, a high level alarm was received while the process was believed to be nonoperational. The alarm was acknowledged on the computer screen, but no further action was taken. Good practice includes evaluating alarms and determining the reason for their activation.

As noted in Section 3.1, the lack of a system to identify the hazards associated with MNT in the continuous process resulted in an inadequate understanding of the sensitivity of the material to heat. When equipment is not operating—and heat is not being removed—MNT must be positively isolated from heat sources to keep the temperature from increasing. A comprehensive training program would have provided another opportunity to assess the hazards and communicate them to operations personnel.

An effective system would have ensured that work practices for isolating equipment contained all necessary steps and were consistently followed, the hazards of the material were communicated, and the procedures codified relevant information. If the steam supply was effectively isolated from the column, the chain of events that led to this incident would not have occurred—even though C-501 was inventoried with material. In addition, if the temperature in the column had been monitored during the time the material inside was heating, operators may have been prompted to take corrective action.

3.4 Maintenance Program and Equipment Integrity

Maintenance activities complement operations and contribute to process safety by ensuring the mechanical integrity of equipment. Maintenance planning and implementation are integral to the safe and efficient operation of process systems. Corrosion, erosion, and fatigue can cause failures in equipment and result in process fluids inadvertently entering equipment or being released.

The importance of preventive maintenance to process safety management cannot be overemphasized. (CCPS, 1995c). An effective preventive maintenance program establishes inspection frequencies for process equipment that is vulnerable to such conditions as corrosion, erosion, and fatigue.

3.4.1 Steam Valves

The MNT system maintenance practices at FCC were less than adequate. There was no evidence that the reboiler steam supply valves had ever been evaluated to determine what maintenance activities were necessary to ensure proper function. Post-incident testing of critical steam isolation valves determined that the valve seats leaked a significant amount of steam in the "closed" position. This uncontrolled and unrecognized steam flow contributed to failure of the #1 MNT column (C-501).

3.4.2 Distillation Column

Interviews with FCC facility personnel revealed that they thought the operating temperature of C-501 was sufficiently high to prevent the accumulation of moisture under external insulation and corrosion of the carbon steel surface. Because of this assumption, FCC did not monitor the condition of the steel. However, the C-501 operating procedure[24] stated that the mid-bed operating temperature is "about 300°F" and the top of the column is "about 140°F."

[24] FCC Document No.1201.003-1003, Revision 11.

CSB found significant external surface corrosion under the upper areas of C-501, including one area where the wall thickness was degraded to 30 percent of its original thickness, with a corresponding reduction in pressure capacity. Although the thinned wall did not cause the incident, it is evidence of the inadequacy in the FCC inspection and maintenance program at that time.

3.5 Overpressure Protection

The #1 MNT column (C-501) was designed, fabricated, and tested in accordance with the American Society of Mechanical Engineers (ASME) pressure vessel code; it had a nameplate rating of 15 psig. A 3-inch nominal pressure safety valve (PSV-502) attached to the overhead vapor line, with a set pressure of 15 psig, provided overpressure protection.

Industry literature and test data show that MNT—if exposed to high temperatures—may violently decompose and generate large volumes of vapor, which may pressurize a column. The PSV must have adequate flow capacity to limit the maximum pressure in a column caused by a runaway reaction.

Determining the relief valve size on a reactive chemical system is complex and requires physical test data on reaction kinetics and flow characteristics. Laboratory test results of MNT are required to determine if the vented contents are a pure gas, a pure liquid, or a combination of both—commonly known as two-phase flow. Pure liquid flow and two-phase flow require a significantly larger flow capacity relief valve.

In the absence of effective safeguards to prevent a runaway reaction, such as safety interlocks and safety work practices (discussed previously), FCC was relying on the PSV for C-501 to provide protection in the event of a thermal decomposition. CSB determined that the capacity of the PSV was inadequate to prevent the overpressurization and catastrophic failure of the column.

As part of thermal stability testing, the CSB contractor estimated that a vessel the size of C-501, with a design pressure of 15 psi, would—if placed on the overhead vapor line—require a 58-inch-diameter relief valve. This excessively large size calls for alternate methods of overpressure protection, including increasing the number or altering the location of relief devices.[25]

Because FCC had no documentation on the design basis for the installed PSV on C-501, CSB was unable to determine the scenario used. The American Petroleum Institute (API) Recommended Practice (RP)-521, *Guide for Pressure-Relieving and Depressuring Systems*, notes that several scenarios must be considered in determining the required capacity of a safety relief valve, including chemical reaction. API states that pressure relief considerations should include estimated vapor generation from both normal and uncontrolled conditions. When a pressure relief device cannot feasibly control pressure, other design strategies may be employed to prevent equipment damage, including automatic shutdown systems.

If FCC had an effective system in place to evaluate the overpressure protection for C-501, it would likely have determined that the relief valve was inadequate. This determination could have led to a comprehensive review of the overpressure protection scheme (i.e., location, size, and number of relief valves) and the addition of safeguards to prevent a decomposition reaction.

3.6 Control Room Construction and Location

Three people in the control room at the time of the incident (5:25 am) were injured by shattering glass from the control room door (Figure 10). The time of day was likely a factor in limiting the number and magnitude of injuries.

The control room for the aniline unit (including the MNT columns) was constructed of masonry block, with sheet metal on the roof and sides. The building was located approximately 50 feet from the #1 MNT column (C-501). The explosion resulted in structural damage to the walls of the building and the roof

[25] The location of relief devices, as well as their sizing, must be considered when evaluating overpressure protection for vessels. Kister (1990) notes that the vapor space at the bottom of a column, just below the packing supports, may be considered as a location for pressure relief devices. In one case, a low-positioned relief prevented overpressure when a device at the top of the column would have been ineffective.

(Figure 9). Several other buildings onsite were damaged, including the administration building, which was located approximately 450 feet from C-501.

Figure 9. Damage to control room roof and door.

Facility siting guidelines—particularly those published by CCPS and API—cover the location and construction of control rooms in the chemical and petrochemical industries. API RP-752 (1995) was developed for facilities covered by the Process Safety Code of the Chemical Manufacturers Association (now the American Chemistry Council [ACC]). FCC was previously a member of CMA and was a member of SOCMA (which adopted the Process Safety Code) at the time of the incident.

API RP-752 includes a step-by-step analysis, beginning with occupancy screening and proceeding to hazard identification, building evaluation, and risk management. It is applicable to both new and existing buildings. The guideline notes that some companies use a range of 200 to 400 personnel hours per week to determine when control room occupancy requires a higher level of analysis. The control room for the FCC aniline unit would typically have had occupancy well in excess of this range. The peak occupancy—or number of personnel that may be exposed in a given period (e.g., such as at a production or safety meeting)—should also be considered.

Another consideration for occupancy is the ability to evacuate a building, though API RP-752 notes that:

> Process materials that have the potential for runaway reactions or chemically or thermally induced decomposition may produce toxic, fire, or explosion effects with little or no warning . . . and . . . building evacuation may not be a viable option.

API RP-752 lists components that can explode due to chemical decomposition as materials of concern. CCPS (1996) notes that processes of concern include those that have the potential for uncontrolled chemical reactions. Methods for calculating the potential consequences of releases include TNT-equivalency, Multi-Energy, and Baker-Strehlow. Hazard evaluation tools, such as the Dow Fire and Explosion Index and the Mond Index, can be used to assist in prioritizing buildings.

The last step in the guidance is to access risk and determine the necessity for preventive or mitigative measures. Preventive measures include adding redundant instrumentation and emergency shutdowns, or altering the process conditions or materials to reduce the potential for runaway reactions. Mitigative measures include eliminating or modifying windows in buildings, or reinforcing or otherwise modifying structures to withstand pressure.

If FCC had performed such an analysis, it would have likely determined that the location and structure of the control room presented a risk to occupants. This conclusion could have led to preventive measures, such as adding instrumentation to columns processing highly energetic material; or mitigative measures, such as removing windows and putting solid doors on the control room, reinforcing walls, or relocating the control room.

3.7 Process Information and Retention of Records

Throughout the investigation, CSB reviewed procedures, testing data, and equipment files. However, some of the information provided by FCC was incomplete or in error. For example, no records were provided for the scenarios considered in sizing the relief valve on the #1 MNT column (C-501). Therefore, CSB was unable to draw conclusions as to failures in the design phase, except to note that subsequent testing of MNT demonstrated that the valve was not sized for a thermal decomposition, which should have been a valid consideration for this material.

CSB also inquired about previous studies regarding the location and structure of the control room. FCC personnel stated that they believe a study was performed, but there was no documentation. CSB sought documentation to support exclusion of the MNT distillation area from requirements of the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) Standard, 29 CFR 1910.119. Again, FCC personnel noted that the evaluation occurred, but there was no documentation. (See Section 3.10 for a discussion of regulatory analysis.)

Upon request, FCC provided two material safety data sheets (MSDS) developed for MNT. The 1992 MSDS noted that MNT: "Decomposes slowly at 392°F." The 1998 MSDS did not include this warning, though it was produced after the 1996 MNT batch project, when testing and literature searches showed that MNT was susceptible to thermal decomposition.

The MNT continuous process was commissioned in the late 1960s, prior to the electronic storage of information. FCC personnel noted that much of the information was lost when people left the company (due to downsizing, resignations, or retirements) and during the sale of a portion of the facility to Albermarle, in which documents were taken offsite for review and in some cases not returned. Personnel also noted that a hurricane destroyed some files.

A comprehensive information management system is essential to maintaining safe operations. Operations personnel must have access to reliable information on the safety of process material and equipment. Neither the MSDSs nor FCC operating procedures contained appropriate cautions about MNT. As noted in Section 3.1, there was no system in place to evaluate the hazards and apply lessons learned from other processes. The lack of a comprehensive system to manage and distribute information, however, meant that even if the hazards had been evaluated and the potential results known, that information may not have been effectively communicated.

3.8 Community Notification System

An effective community notification system alerts people to the fact that an incident occurred and informs them when the situation is over. As part of the notification system or educational campaign, people are instructed on the appropriate steps to take to protect themselves.

CSB evaluated the emergency response and community notification system. This effort included a meeting with the local emergency planning committee (LEPC) and a community meeting for local residents. It also included surveying several industrial areas with residential neighbors to determine good practices in community notification and emergency response. The survey revealed multiple methods of communicating information about chemical incidents, including sirens and reverse 9-1-1 systems. Local residents in those areas had been trained on shelter-in-place procedures.

CSB determined that the Jackson County public communication system was ineffective. A shelter-in-place was called, but it was not effectively communicated to local residents by the media. This should have been a necessary step to ensure that appropriate actions were taken by residents and neighboring companies. There is also a need for improved community education and training on what steps to take in the event of a shelter-in-place. Although post-incident monitoring and analysis of wind direction indicated that the smoke moved away from residential areas, timely communication with residents would have decreased their anxiety.

Numerous County, State, and Federal agencies and corporate neighbors responded to this incident, including local fire and police, the Chevron refinery fire department, the U.S. Coast Guard, and the County Sheriff. Police and fire personnel quickly closed Bayou Cassotte Industrial Road. The sheriff issued the order to shelter-in-place. The Federal Aviation Administration established a "no fly zone" over the facility and surrounding area to safeguard aircraft. State and Federal EPA arrived onsite and established environmental monitoring stations outside the perimeter of the facility.

The FCC night-shift supervisor assumed the role of onsite incident commander. He coordinated facility firefighting, accounted for employees, and directed ambulances to the three injured employees.

FCC operators quickly shut down and isolated all process and plant utility units. Based on site interviews of first responders and unit operators, the response to the initial explosion and fire was rapid.

3.9 Review of Previous/Similar Incidents

3.9.1 Previous Incidents at Pascagoula Facility

FCC experienced an explosion and fire in a batch process under development for a third party in 1986. A runaway self-heating reaction in a process used to distill meta-chloroaniline overwhelmed equipment relief devices. The incident involved a runaway reaction and overpressurization of equipment in a column that had no special provisions to mitigate a thermal runaway. The column was destroyed, and debris was propelled offsite.

One of the recommendations was to perform hazard analyses of existing processes. FCC did not apply lessons learned from this event to the MNT distillation system. If a thorough review of the safety systems and overpressure protection for distillation columns had been conducted at that time, the inadequacies in column design and operation may have been identified and actions taken to lessen the likelihood of the October 13 incident.

3.9.2 Review of Similar Incidents in Industry

CSB reviewed incidents involving similar materials or similar causal circumstances. Each of the following incidents involved material that was held at temperatures thought to be safe, but which proved to be thermally unstable.

Hickson & Welch Ltd, 1992

A September 21, 1992, incident at Hickson & Welch Ltd, Castleford, United Kingdom, killed five workers (Health and Safety Executive [HSE], 1994). It involved similar materials and also resulted in an explosive thermal decomposition. Workers attempting to clean a still used in an MNT distillation process applied steam to the still for 3 hours to soften accumulated sludge, which was rich in dinitrotoluenes and nitro cresols.

HSE determined that the residue initiated a runaway reaction, which caused a deflagration and intense fire. Among the findings of HSE was that the sludge contained organic nitro compounds; it was known that exposing such compounds to high temperatures or to moderately elevated temperatures over an extended time could cause a thermal decomposition. HSE further found that upper management knew of these hazards from previous incidents at the plant. The company had in place a system of thermal stability testing that was intended to supply managers with the information necessary to safely operate the distillation plant. However, there was no attempt on the part of Hickson & Welch management to characterize the sludge material or the hazards related to its removal, specifically potential thermal instability.

Union Carbide, 1972

On August 7, 1972, at a Union Carbide facility located in Institute, West Virginia, a transfer line containing dinitrotoluene (DNT)[26] exploded (Bateman, Small, and Snyder, 1974). This event was followed by numerous other explosions and small secondary fires, resulting in one minor injury. The transfer line was a 300-foot-long, 2-inch pipeline located both above and below ground. It was fitted with steam jacketing to maintain a pressure of 15 to 20 psi.

The knowledge at the time was that this material could be safely transferred or held stagnant under the operating conditions thought to be present. Prior to this incident, the material had been held in the line for about 10 days.

Internal investigation concluded that one of the steam reduction stations controlling the heat addition malfunctioned, allowing superheated steam to heat the material to about 210°C. Union Carbide personnel knew that DNT would violently decompose at temperatures above 270°C, but they believed that the steam temperature did not exceed 210°C. Numerous tests were conducted to investigate the time–temperature relationship. It was determined that slightly elevated temperatures over time did influence the stability of DNT. This finding resulted in the reduction of maximum operating temperatures, the reduction of holding times for DNT, and the addition of several continuous temperature measurements along the transfer line.

American Cyanamid Co., 1969

In October 1969, an explosion occurred at an American Cyanamid Co. plant in a process that produced para-nitrometacresol (PNMC), which was used in making pesticides (Dartnell and Ventrone, 1971). The explosion killed one worker, split the 3,000-gallon stainless-steel storage tank into five pieces, destroyed

[26] Dinitrotoluene is a mononitrotoluene with an additional nitro group added to the molecule.

equipment within 25 feet of the tank, and started a small fire. The tank contained about 1,500 gallons of PNMC.

The melting point of PNMC is 127°C; the temperature on the tank was maintained to keep the contents at 135°C. During design, pure PNMC was tested and showed no instability at temperatures as high as 200°C. The incident investigation found that the temperature of PNMC inside the tank was held at an elevated level of 154°C for 3 days prior to the explosion.

Thermal stability testing performed post incident found PNMC to be unstable at temperatures above its melting point. In terms of temperature and time, its instability was directly related to the heat to which it had been subjected. The key conclusion was that new process streams must be tested under conditions that are present in actual process operations.

Collectively, these incidents demonstrate that aromatic nitro compounds are susceptible to thermal decomposition and may react at temperatures lower than the predicted "onset temperature"[27] if they are held at elevated temperatures for an extended time.

[27] The onset temperature is that at which an instantaneous, generally violent decomposition is expected to occur.

3.10 Regulatory Analysis

3.10.1 Process Safety Management Standard

The OSHA PSM Standard, Process Safety Management of Highly Hazardous Chemicals (29 CFR 1910.119), is intended to prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. These regulations apply to processes[28] containing more than a threshold quantity of any one of 137 OSHA-listed "highly hazardous chemicals." Chemicals are listed based on their toxic or reactive properties. Flammable substances are also covered as a class.

Thirty-eight of the 137 chemicals are considered highly reactive based on a National Fire Protection Association (NFPA) instability rating of "3" or "4." The PSM Standard does not list any MNT isomers as highly hazardous chemicals. MNT is also not considered flammable because it has a flash point greater than 100°F. MNT has an NFPA flammability and reactivity rating of "1"[29] (NFPA, 1996; pp 704-707).

The PSM Standard includes in the definition of "process" any group of interconnected vessels. MNT is made by reacting toluene with sulfuric and nitric acids. The material flows to an atmospheric storage tank to await separation in the toluene stripper and then to the distillation columns to separate the isomers. Toluene is considered flammable according to the PSM Standard. However, FCC did not consider the MNT process to be covered by the standard because previous evaluations determined that less than

[28] OSHA defines a process as any activity involving a highly hazardous chemical, including any use, storage, manufacturing, handling, or onsite movement of such chemicals, or any combination of these activities. For purposes of this definition, any group of vessels that is interconnected, and separate vessels that are located such that a highly hazardous chemical could be involved in a potential release, are considered to be a single process (29 CFR 1910.119(b)).

[29] The NFPA hazard rating system is intended to provide basic information for firefighters and emergency responders. It rates fire, health, and reactivity on a "0" to "4" scale.

10,000 pounds of toluene was involved. Downstream of the atmospheric storage tank, the quantity of toluene did not exceed the 10,000-pound threshold.[30]

3.10.2 EPA Risk Management Program

EPA promulgated the Risk Management Program (RMP) regulation, Accidental Release Prevention Requirements (40 CFR 68), in 1996. It requires facilities to submit risk management plans to EPA. The RMP regulation contains several process safety elements that are similar to the OSHA PSM Standard. However, among the differences is that the RMP regulation specifically lists flammables, while the PSM Standard treats them as a class of chemicals. FCC submitted risk management plans for "covered" materials that were onsite in threshold quantities (i.e., for ammonia, oleum (fuming sulfuric acid), and formaldehyde). MNT is not on the list of RMP-covered chemicals.

3.10.3 Other Regulatory Standards

OSHA has established a standard on controlling hazardous energy (lockout/tagout)[31] that applies to all industries and workplaces. Its purpose is to prevent unexpected energization, startup, or release of stored energy when personnel operate, service, or maintain machinery or equipment. The standard requires employers to establish an energy control program and apply lockout/tagout[32] devices or energy isolation devices, or to otherwise disable such equipment.

[30] This conclusion is based on an interpretation by an administrative law judge who ruled that PSM coverage does not extend to stored flammables in atmospheric tanks even if they are connected to a process. OSHA has not challenged this decision. U.S. Secretary of Labor v. Meer Corporation, OSHRC Docket No. 95-0341, 1995.

[31] 29 CFR 1910.147, The Control of Hazardous Energy (lockout/tagout).

[32] OSHA defines "lockout" as the placement of a lockout device on an energy-isolating device, in accordance with an established procedure, to ensure that the energy-isolating device and the equipment being controlled cannot be operated until the lockout device is removed. OSHA defines "tagout" as the placement of a tagout device on an energy-isolating device, in accordance with an established procedure, to ensure that the energy-isolating device and the equipment being controlled cannot be operated until the tagout device is removed (29 CFR 1910.147).

Although the Pascagoula facility had a program in place to comply with OSHA lockout/tagout requirements, the steam line was not positively isolated when the #1 MNT column (C-501) sat idle with material inside.

3.10.4 OSHA Investigation

OSHA investigated the Pascagoula facility following the October 13 explosion and issued citations to FCC related to the PHA for the anhydrous ammonia unit, located near the MNT unit. OSHA determined that the PHA was deficient because it did not identify "any previous incident which had a likely potential for catastrophic consequences." OSHA noted in this citation that a bleed valve in the ammonia unit had been left open during shutdown and was not identified as needing to be checked prior to startup, which resulted in a release of ammonia. OSHA also noted that the PHA did not address appropriate detection methodologies to provide early warning of releases, nor did it consider the consequences of the failure of engineering and administrative safeguards. One citation noted that FCC did not "establish and implement" mechanical integrity procedures for columns and piping to and from the anhydrous ammonia storage tank.

OSHA also issued a lockout/tagout citation under 29 CFR 1910.147, noting that the DBB energy-isolating devices called for in the company shutdown procedures were not physically installed to control steam energy sources.

3.10.5 Previous CSB Recommendations on Reactive Chemicals

In April 1998, CSB investigated the explosion and fire at the Morton International, Inc., facility in Paterson, New Jersey, which was caused by a runaway chemical reaction. CSB identified the lack of a reactive hazard management system as a key issue in that incident. Among the CSB recommendations to Morton were revalidating PHAs, evaluating pressure relief requirements, reviewing the need for alarms and safety instrumentation, and sharing process safety information with relevant units of the company.

CSB also made recommendations to both OSHA and EPA to issue joint guidelines regarding reactive chemical process hazards, and to participate in a CSB investigation of such hazards. This hazard investigation report, entitled *Improving Reactive Hazard Management*, was presented to the Board at a public meeting in September 2002 (USCSB, 2002). The Board unanimously approved the recommendations to improve reactive chemical safety. Among these recommendations were that OSHA: ". . . amend the Process Safety Management (PSM) Standard . . . to achieve more comprehensive control of reactive hazards" by broadening the application of PSM, requiring that multiple sources be consulted when compiling process safety information, and augmenting the PHA element to explicitly require an evaluation of reactive hazards (USCSB, 2002; p. 101).

CSB also recommended that EPA revise the RMP regulation (40 CFR Part 68) to explicitly cover catastrophic reactive hazards that may affect the public. Other recommendations were made to CCPS, ACC, and SOCMA to publish guidelines, expand the Responsible Care Process Safety Code, and develop a reporting system for reactive incidents (USCSB, 2002; pp. 102–104).

The FCC incident serves to reemphasize the need to implement CSB recommendations from the reactive hazard investigation. This incident involved a thermal decomposition in a process that had not been properly evaluated. As noted in Section 3.1, in a 1996 evaluation of a different unit processing the same material, FCC included several of the essential elements for a comprehensive reactive chemicals program, such as testing and literature searches to determine the stability of the material and a hazard analysis that included safety recommendations. However, FCC did not consistently practice this hazard evaluation methodology, and there was no system in place to ensure that important hazard information was shared among different processing units.

As noted in Section 3.1, good practice guidelines prompt facilities to evaluate hazards in highly energetic processes. If FCC had conducted such an evaluation of the continuous MNT distillation process (as for the batch MNT process), the potential hazards would have been better understood and preemptive actions could have been taken in the areas of work and maintenance practices.

3.10.6 Good Management Practices

FCC was an active member of SOCMA at the time of the incident. In 1990, SOCMA adopted the chemical industry's Responsible Care initiative as its primary performance improvement program. Although not a regulatory requirement, Responsible Care represents the chemical industry's commitment to the continuous improvement of environmental, health, and safety performance. All active members are required to sign the Responsible Care Guiding Principles and to submit annual reports of their progress in implementing each of the codes, which include process safety and employee health and safety.[33]

The Process Safety Code was designed to prevent fires, explosions, and accidental chemical releases. To implement the code, SOCMA active member companies are required to establish an ongoing safety program that includes measurement of performance, audits of conformity, and a written safety policy. Companies also conduct safety reviews of all new and modified facilities before startup, have maintenance and inspection programs, and must document and have up-to-date safety information on process design and procedures.

CSB requested the most recent Responsible Care audit performed by FCC prior to the incident and was provided with the self-evaluation audit for the Process Safety Code conducted in February 2001. The code requires companies to have management practices in place to ensure, among other items—periodic assessment and documentation of process hazards, complete documentation on the hazards of materials, and sufficient layers of protection to prevent a single failure from leading to a catastrophic event.

[33] The Responsible Care elements referenced herein are those in place when the 2001 audit was performed. The elements have recently been revised.

Although all the code elements except one were marked as having a management practice in place,[34] the CSB investigation uncovered significant gaps in these areas, as previously discussed.

As part of the reactive hazard investigation, CSB also recommended that ACC expand the Responsible Care Process Safety Code to emphasize the need for safe management of reactive hazards (USCSB, 2002; pp. 103–104).

[34] The code element regarding use of community awareness and emergency response to ensure that public comments are considered in design and safety was marked as "reassessing management practice implementation."

4.0 Root and Contributing Causes

4.1 Root Causes

1. **The FCC Pascagoula facility did not have an adequate system for evaluating the hazards of processing mononitrotoluene (MNT) in its continuous process and did not apply lessons learned from hazard analyses conducted on similar processes in the plant.**

- Nitrotoluenes are unstable and decompose energetically under high-temperature conditions. The facility did not have a formal system to evaluate the thermal instabilities of processing this material so that the potential hazards could be understood. FCC had never completed a formal hazard analysis for the continuous MNT unit to evaluate the specific hazards of handling this material, including leaving it in equipment for an extended time during shutdown, short- and long-term shutdown procedures, and response to deviations from normal operating conditions.

- The facility became aware of the hazards of allowing MNT to be exposed to elevated temperatures for an extended time during a batch project in 1996, but the lessons learned (including operating considerations and the addition of safety interlocks) were not applied to the existing MNT columns.

- Because a formal hazard evaluation was not performed and the potential hazards were not understood, process safety information—including MSDSs and standard operating procedures—did not provide adequate warnings of the potential thermal instability of MNT.

2. FCC did not have a system to ensure that the #1 MNT column (C-501) was equipped with sufficient layers of protection to prevent a catastrophic release.

- C-501 did not contain critical alarms, such as high temperature alarms, to warn of deviations from safe operation.
- C-501 did not have safety interlocks to shut down the heat source to the column in the event of high temperature and to return the process to a functionally safe state.
- C-501 did not have appropriately designed overpressure protection in the event of a thermal decomposition of MNT.

3. The Pascagoula facility had no effective system for ensuring consistent work practices when isolating equipment.

- Such a system would specify correct procedures and ensure that all necessary steps are followed. Although personnel stated that proper isolation included double blocking and bleeding the steam line to C-501, these steps were not specifically included in the procedures and were not followed prior to the incident.
- Operating procedures for C-501 did not contain warnings or cautions concerning process chemicals and the consequences of deviations from operating limits.
- Operating procedures did not contain instructions on how to perform an emergency shutdown for all foreseeable causes, to ensure proper isolation, or to continue monitoring critical parameters while the column was shut down.
- Work practices at the time of the incident did not include blinding the steam line, which would have isolated the line from the column.

- Training of operations personnel did not include information on the hazards of leaving MNT at elevated levels for an extended time, which would have further emphasized the necessity to ensure proper isolation of heat sources to the column when heat was not being removed.

4. **FCC did not have an adequate program to prevent leakage from isolation valves in the steam line connected to the #1 MNT column (C-501).**

- The steam supply valves had not been evaluated to determine what maintenance activities were appropriate to ensure proper function.

- Post-incident analysis revealed that corrosion and erosion caused the leakage in two manual valves in the steam line to the reboilers.

4.2 Contributing Causes

1. **FCC did not have a system to evaluate the structural integrity of the control room or its proximity to the process.**[35]

The control room for the MNT unit—which had windows and was not reinforced to withstand overpressure—was located approximately 50 feet from C-501. Three employees who sought refuge in the control room at the time of the incident were injured by broken glass.

[35] It is important to note that, though the siting of the control room and the ineffectiveness of the community notification system did not cause the incident, they contributed to its consequences—including onsite injuries and anxiety within the local community.

2. Jackson County did not have an effective system to alert residents about potentially catastrophic incidents and appropriate responses.

The explosion and fire caused significant concern among residents in the surrounding community. Concussion damage was observed offsite, and debris from the column was thrown offsite. The community notification system did not adequately warn residents that an incident was ongoing, explain how to shelter-in-place, or let them know when the emergency had subsided.

5.0 Recommendations

DuPont Corporation

Conduct audits to ensure that the First Chemical Pascagoula Facility addresses the issues detailed below, under "DuPont–First Chemical Pascagoula Facility." Communicate results of these audits to the workforce. (2003-01-I-MS-R1)

DuPont–First Chemical Pascagoula Facility

1. Establish a program for conducting process hazard analyses of processes involving reactive materials. (2003-01-I-MS-R2)

2. Evaluate the need for layers of protection and install appropriate safeguards, such as alarms and interlocks, to reduce the likelihood of a runaway reaction and catastrophic release of material. (2003-01-I-MS-R3)

3. Review and revise as necessary procedures for units that process highly energetic material, effectively communicate the updated procedures, and train workers appropriately. Revised procedures should include: (2003-01-I-MS-R4)

   - Specific steps for isolation of energy sources.
   - Warnings and cautions concerning process chemicals and consequences of deviations from operating limits.
   - Critical operating limits and guidance when the limits are exceeded.
   - Instruction on how to perform a shutdown for all foreseeable causes, to ensure proper isolation, and to continue monitoring critical parameters (such as temperature) while the

column is shut down; in addition, review conditions under which material must be deinventoried (such as during extended shutdowns).

4. Conduct a facility-wide survey of pressure vessels to ensure that all equipment that processes reactive materials has appropriate overpressure protection. (2003-01-I-MS-R5)

5. Identify equipment critical to safe operation of processes containing reactive materials. Upgrade the maintenance program and establish inspection schedules to ensure the integrity of such equipment. (2003-01-I-MS-R6)

6. Survey and take appropriate action to ensure that buildings occupied by plant personnel are of adequate construction and are located so as to protect people inside in the event of an explosion in equipment processing reactive materials. (2003-01-I-MS-R7)

Jackson County Board of Supervisors
Jackson County Emergency Management Agency
Jackson County Local Emergency Planning Committee

1. Update the community notification system to: (2003-01-I-MS-R8)

    - Immediately alert residents in the Moss Point community when an incident occurs that could affect their health and safety.
    - Determine when a community response should be initiated.
    - Communicate the nature of the incident and the appropriate response by residents.
    - Alert residents when the incident is over (i.e., the all-clear has sounded).

2. Conduct an awareness campaign to educate residents on the proper steps for a shelter-in-place and orderly evacuation. (2003-01-I-MS-R9)

American Chemistry Council (ACC)

1. Amend the Technical Specifications guidelines in the Responsible Care Management System to explicitly require facilities to identify findings and lessons learned from process hazard analyses and incident investigations in one unit and apply them to other equipment that processes similar material. (2003-01-I-MS-R10)

2. Ensure that ACC members understand the audit requirements of Responsible Care and accurately identify and address gaps in facility process safety programs. (2003-01-I-MS-R11)

3. Communicate the findings of this report to your membership. (2003-01-I-MS-R12)

Synthetic Organic Chemical Manufacturers Association (SOCMA)

1. Amend the Technical Specifications in the Responsible Care Management System to explicitly require facilities to identify findings and lessons learned from process hazard analyses and incident investigations in one unit and apply them to other equipment that processes similar material. (2003-01-I-MS-R13)

2. Ensure that SOCMA members understand the audit requirements of Responsible Care and accurately identify and address gaps in facility process safety programs. (2003-01-I-MS-R14)

3. Communicate the findings of this report to your membership. (2003-01-I-MS-R15)

By the

U.S. Chemical Safety and Hazard Investigation Board

Carolyn W. Merritt
Chair

John S. Bresland
Member

Gerald V. Poje, Ph.D.
Member

Isadore Rosenthal, Ph.D.
Member

Andrea Kidd Taylor, Dr. P.H.
Member

October 15, 2003

6.0 References

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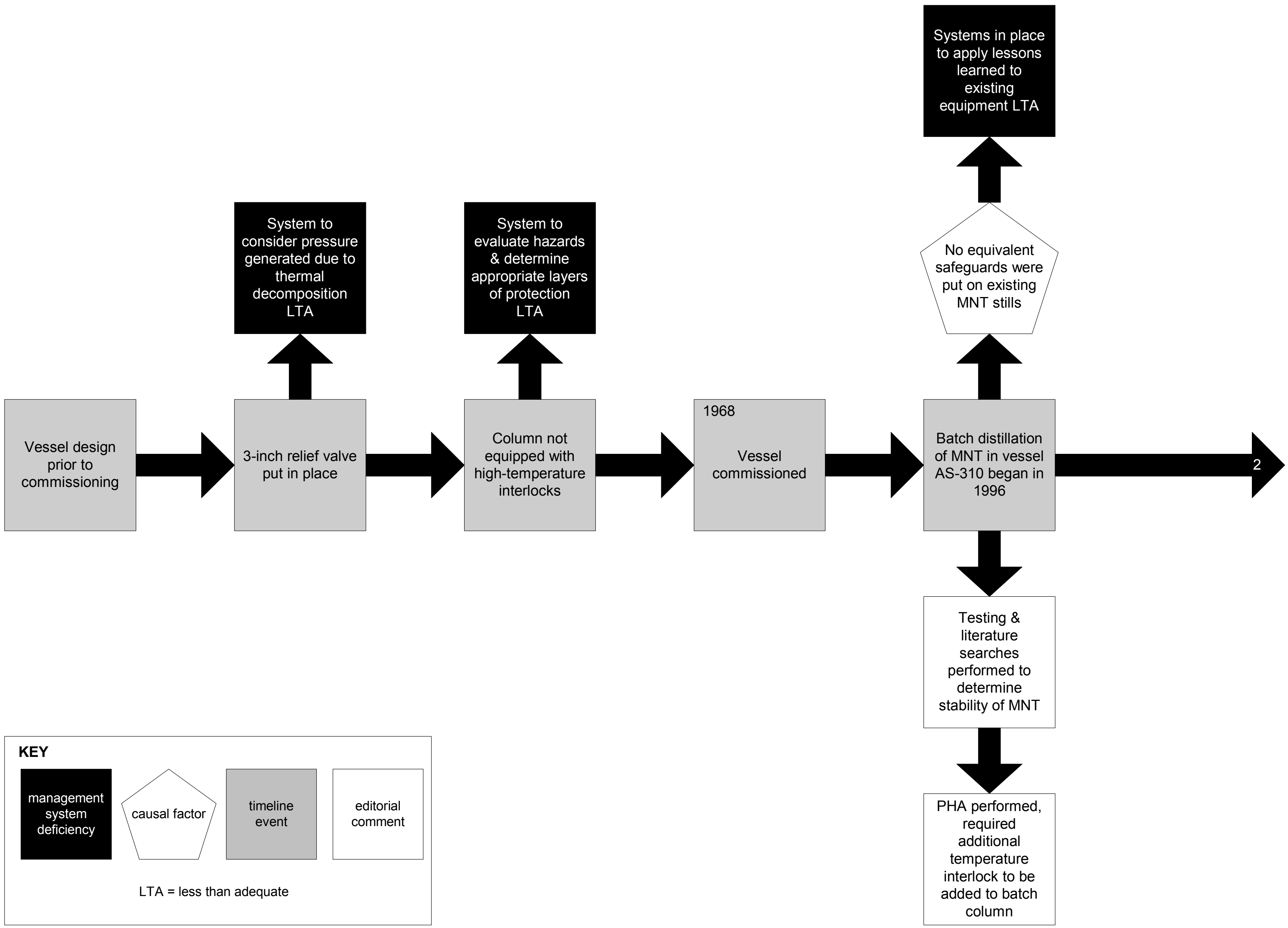
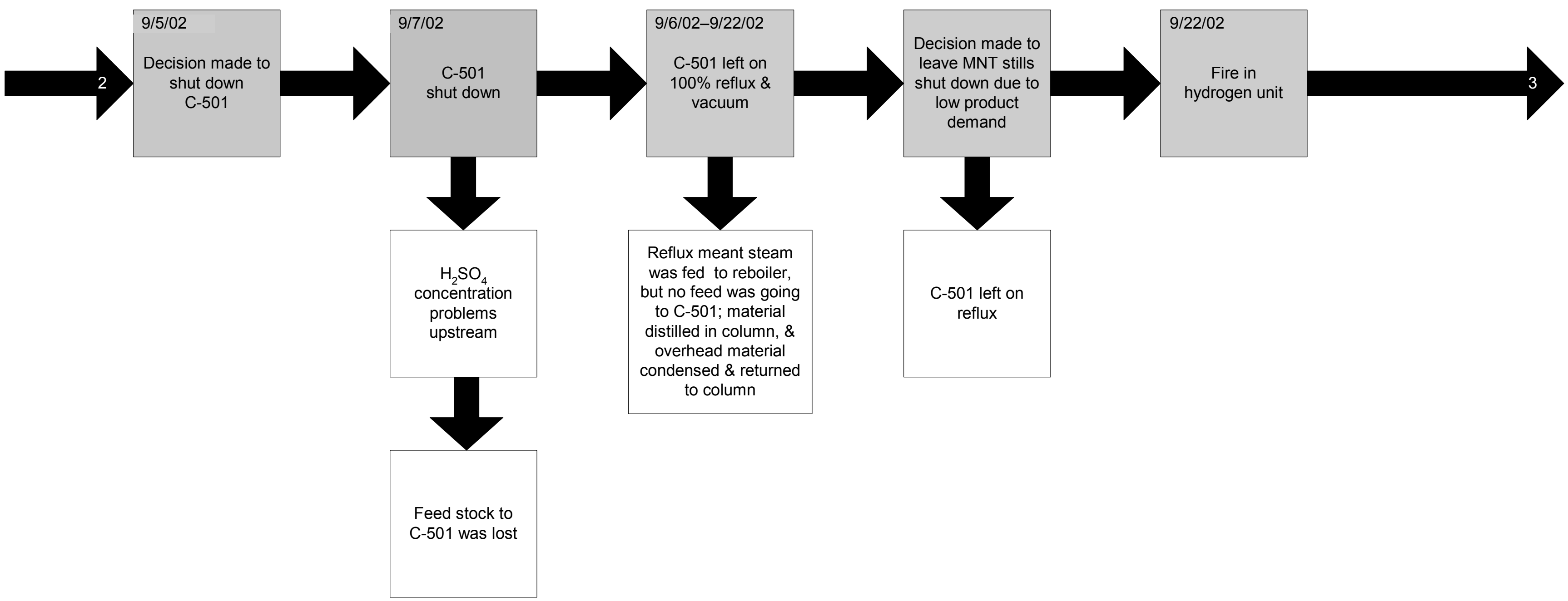
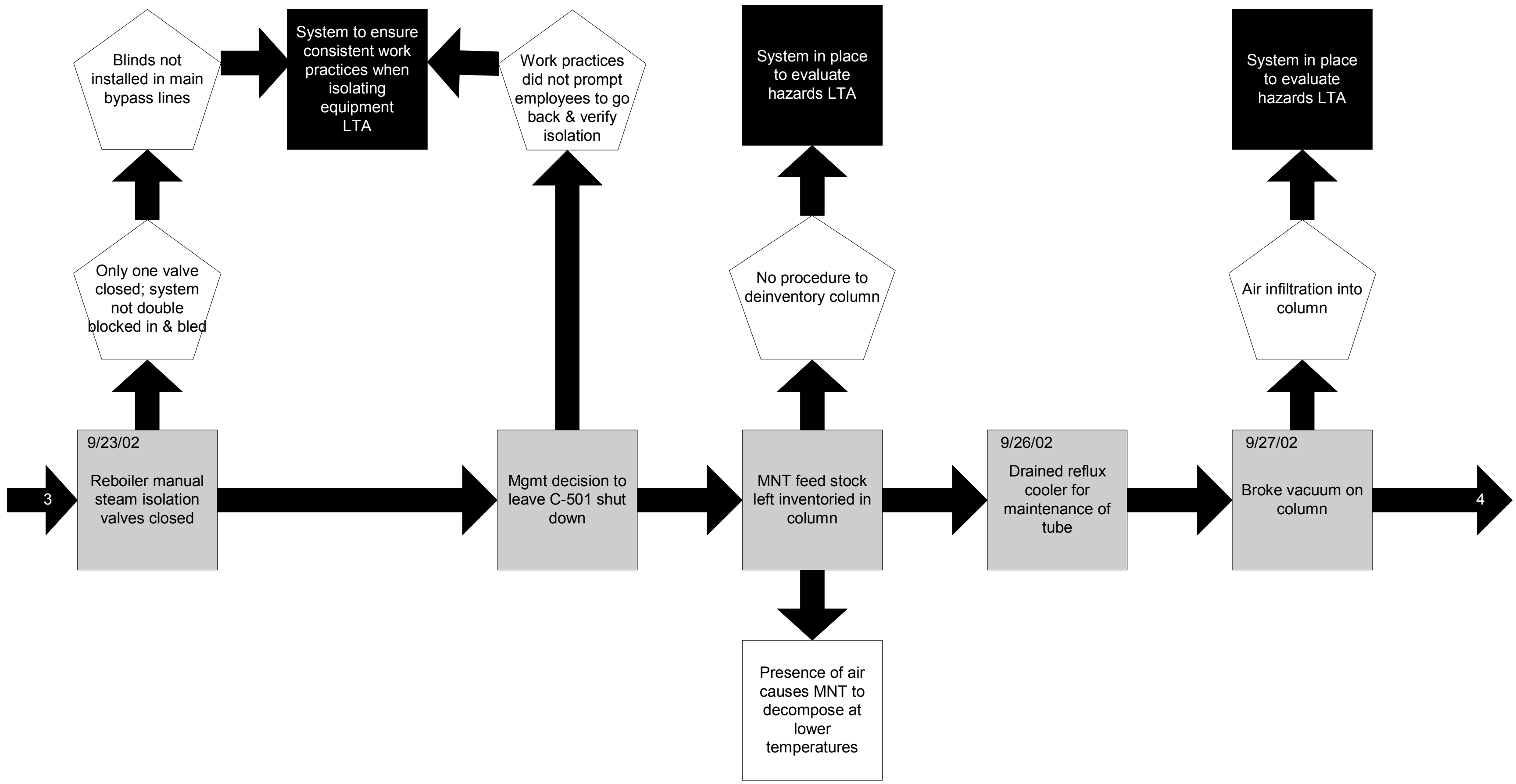
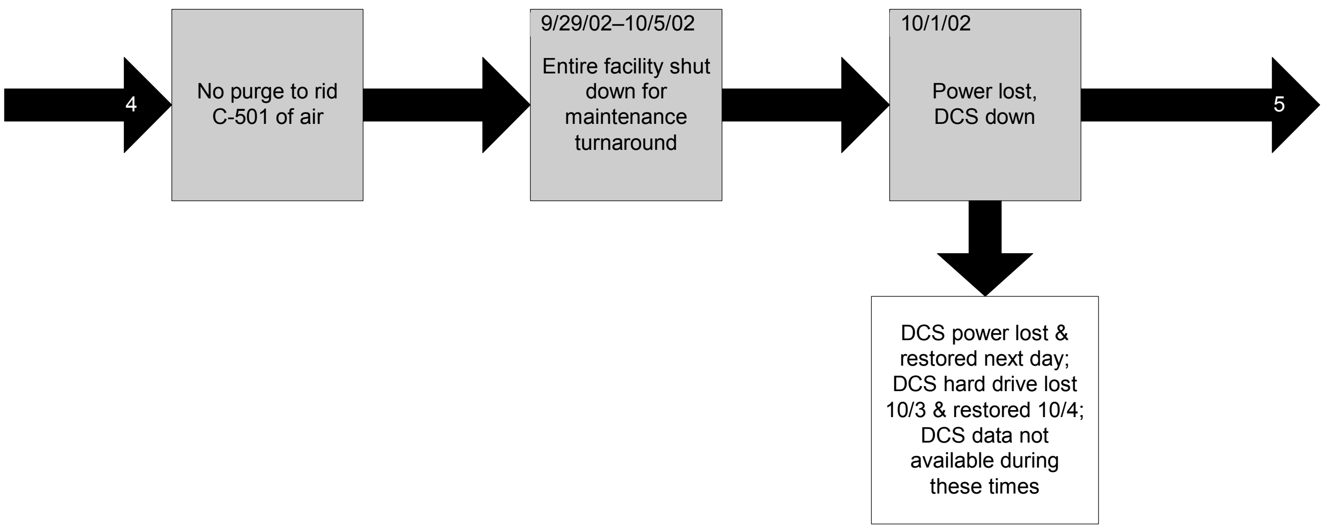
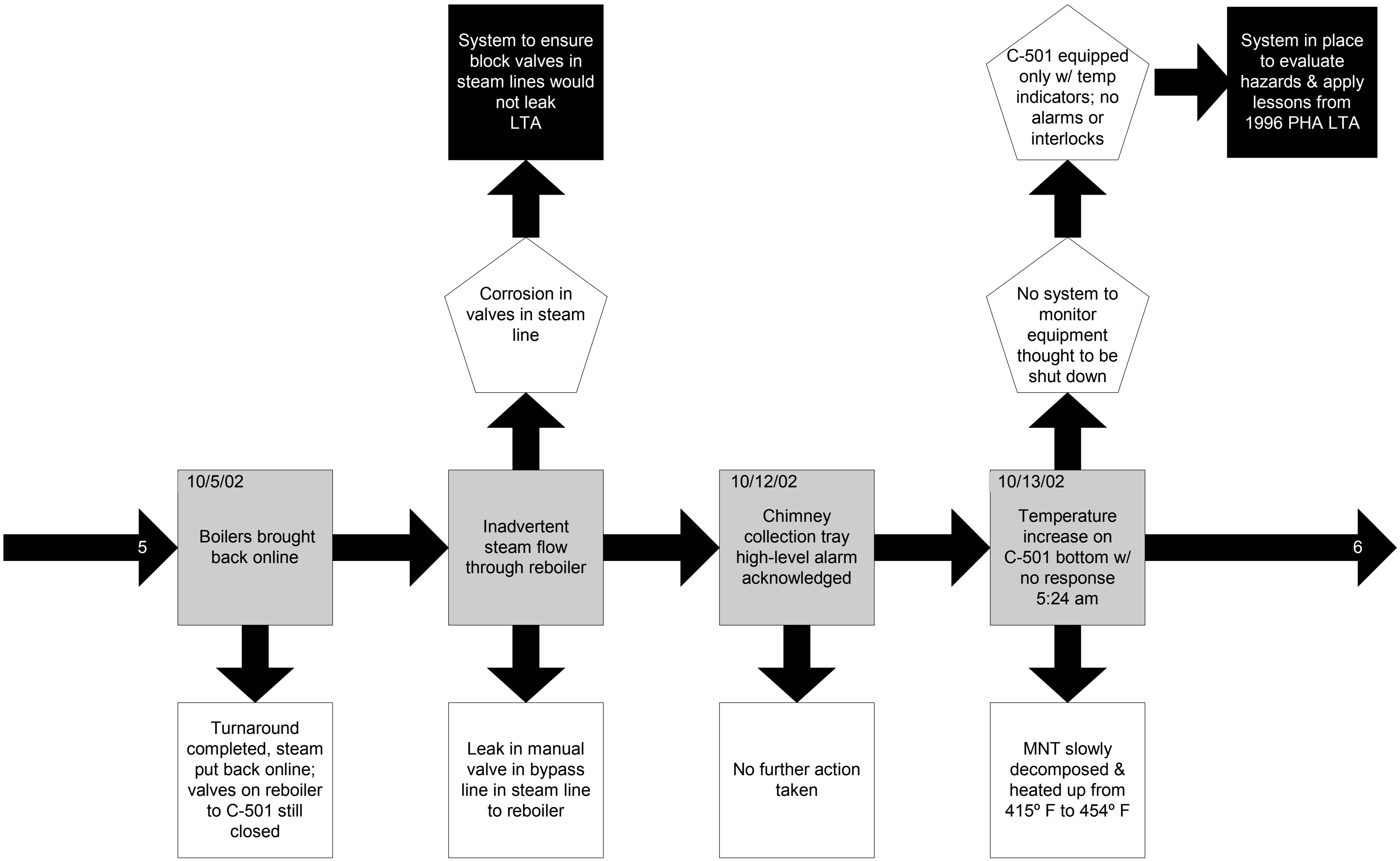
APPENDIX A: Causal Factors Diagram

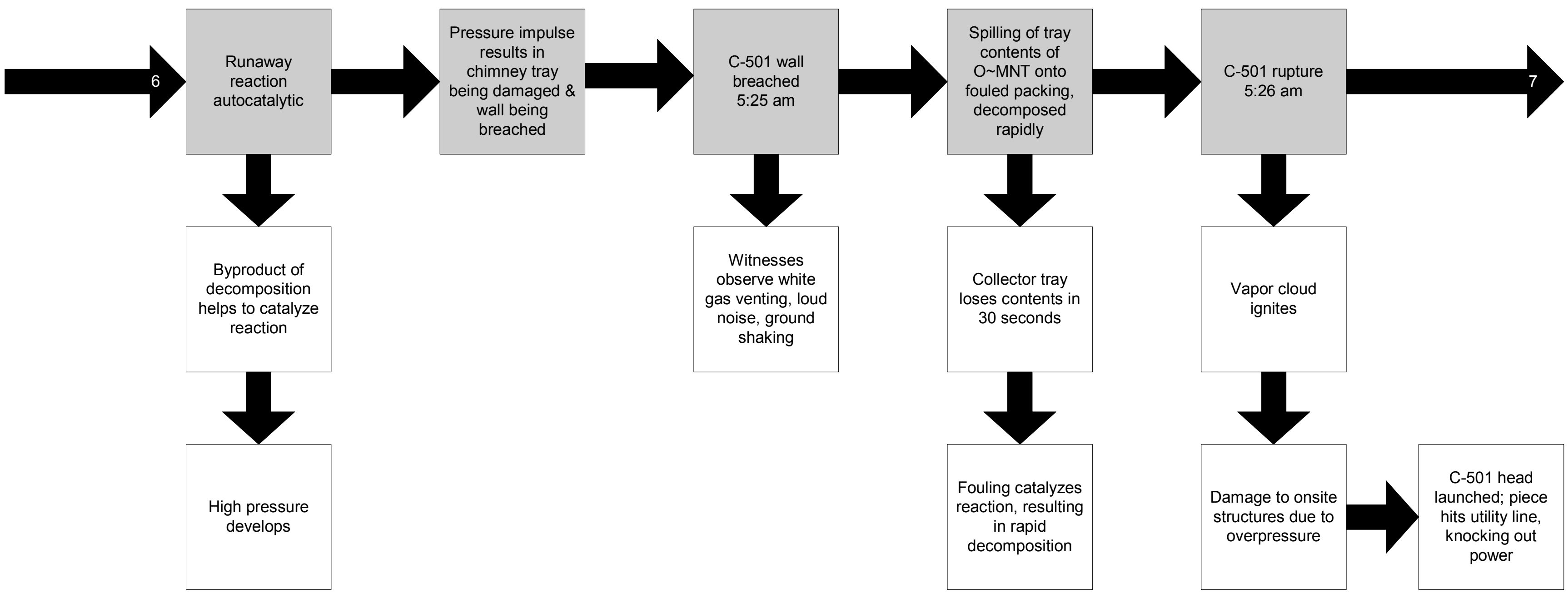

Systems in place to apply lessons learned to existing equipment LTA
System to consider pressure generated due to thermal decomposition LTA
System to evaluate hazards & determine appropriate layers of protection LTA
No equivalent safeguards were put on existing MNT stills
Vessel design prior to commissioning
3-inch relief valve put in place
Column not equipped with high-temperature interlocks
1968
Vessel commissioned
Batch distillation of MNT in vessel AS-310 began in 1996
2
Testing & literature searches performed to determine stability of MNT
PHA performed, required additional temperature interlock to be added to batch column
KEY
management system deficiency
causal factor
timeline event
editorial comment
LTA = less than adequate

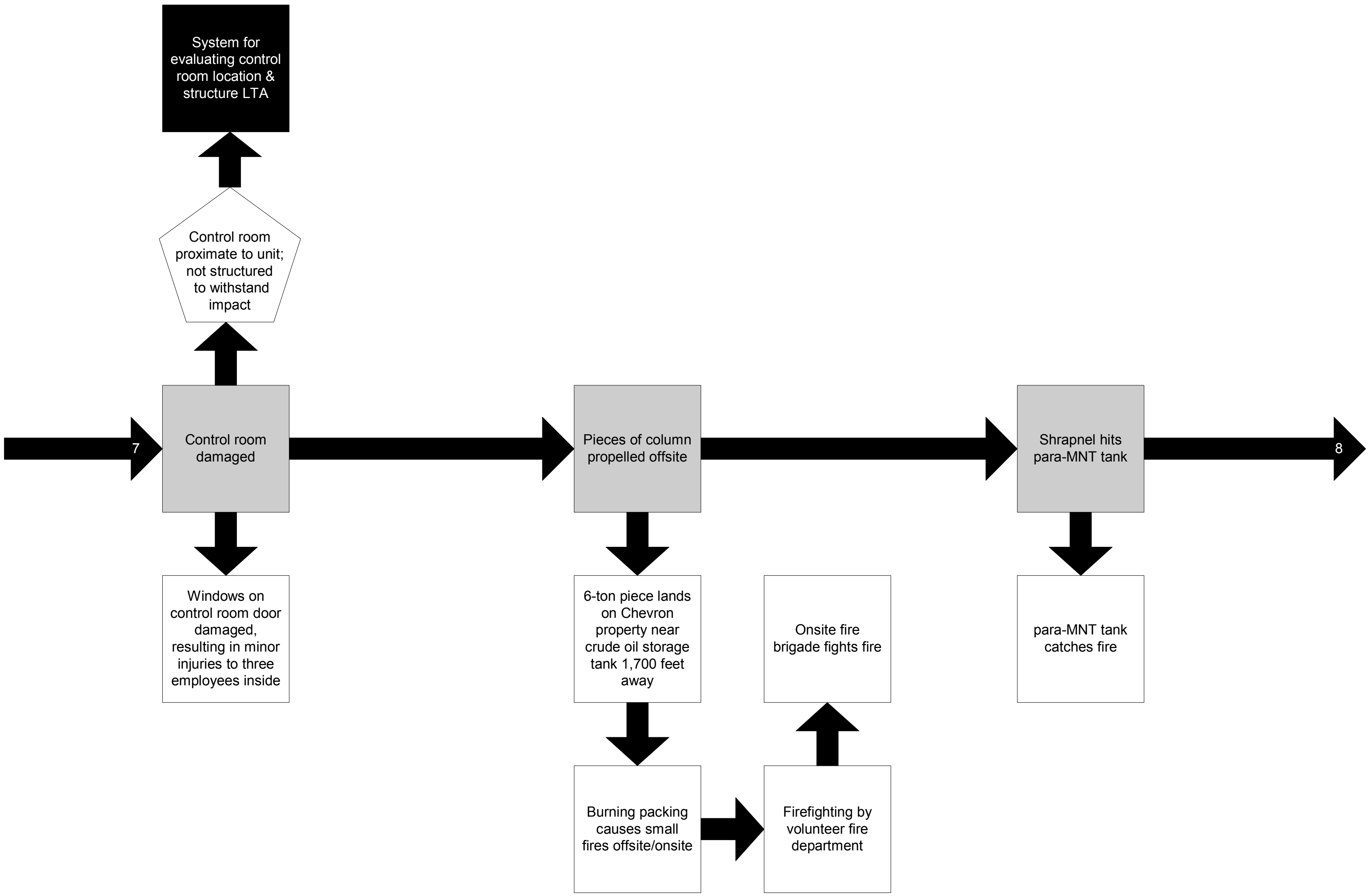

2
9/5/02
Decision made to shut down C-501
9/7/02
C-501 shut down
9/6/02–9/22/02
C-501 left on 100% reflux & vacuum
Decision made to leave MNT stills shut down due to low product demand
9/22/02
Fire in hydrogen unit
3
H_2SO_4 concentration problems upstream
Feed stock to C-501 was lost
Reflux meant steam was fed to reboiler, but no feed was going to C-501; material distilled in column, & overhead material condensed & returned to column
C-501 left on reflux

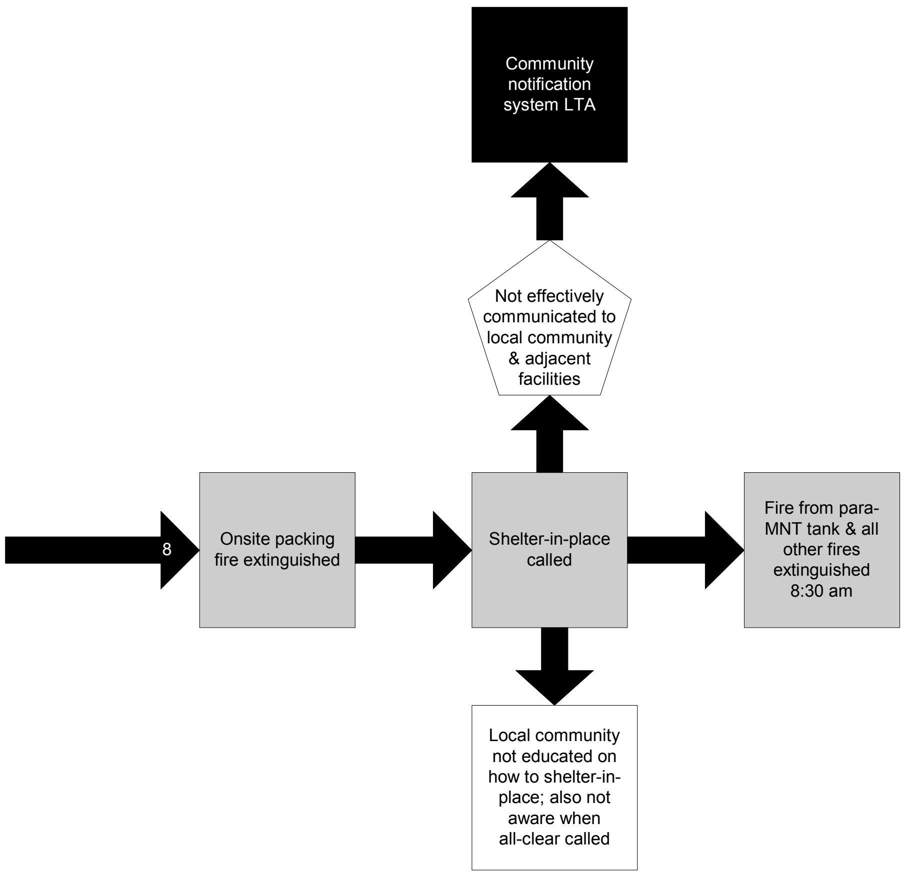

Blinds not installed in main bypass lines
System to ensure consistent work practices when isolating equipment LTA
Work practices did not prompt employees to go back & verify isolation
System in place to evaluate hazards LTA
System in place to evaluate hazards LTA
Only one valve closed; system not double blocked in & bled
No procedure to deinventory column
Air infiltration into column
3
9/23/02
Reboiler manual steam isolation valves closed
Mgmt decision to leave C-501 shut down
MNT feed stock left inventoried in column
9/26/02
Drained reflux cooler for maintenance of tube
9/27/02
Broke vacuum on column
4
Presence of air causes MNT to decompose at lower temperatures


4
No purge to rid C-501 of air
9/29/02–10/5/02
Entire facility shut down for maintenance turnaround
10/1/02
Power lost, DCS down
5
DCS power lost & restored next day; DCS hard drive lost 10/3 & restored 10/4; DCS data not available during these times


System to ensure block valves in steam lines would not leak LTA
C-501 equipped only w/ temp indicators; no alarms or interlocks
System in place to evaluate hazards & apply lessons from 1996 PHA LTA
Corrosion in valves in steam line
No system to monitor equipment thought to be shut down
5
10/5/02 Boilers brought back online
Inadvertent steam flow through reboiler
10/12/02 Chimney collection tray high-level alarm acknowledged
10/13/02 Temperature increase on C-501 bottom w/ no response 5:24 am
6
Turnaround completed, steam put back online; valves on reboiler to C-501 still closed
Leak in manual valve in bypass line in steam line to reboiler
No further action taken
MNT slowly decomposed & heated up from 415º F to 454º F


6
Runaway reaction autocatalytic
Pressure impulse results in chimney tray being damaged & wall being breached
C-501 wall breached 5:25 am
Spilling of tray contents of O~MNT onto fouled packing, decomposed rapidly
C-501 rupture 5:26 am
7
Byproduct of decomposition helps to catalyze reaction
High pressure develops
Witnesses observe white gas venting, loud noise, ground shaking
Collector tray loses contents in 30 seconds
Fouling catalyzes reaction, resulting in rapid decomposition
Vapor cloud ignites
Damage to onsite structures due to overpressure
C-501 head launched; piece hits utility line, knocking out power


System for evaluating control room location & structure LTA
Control room proximate to unit; not structured to withstand impact
7
Control room damaged
Pieces of column propelled offsite
Shrapnel hits para-MNT tank
8
Windows on control room door damaged, resulting in minor injuries to three employees inside
6-ton piece lands on Chevron property near crude oil storage tank 1,700 feet away
Onsite fire brigade fights fire
para-MNT tank catches fire
Burning packing causes small fires offsite/onsite
Firefighting by volunteer fire department


Community notification system LTA
Not effectively communicated to local community & adjacent facilities
8
Onsite packing fire extinguished
Shelter-in-place called
Fire from para-MNT tank & all other fires extinguished 8:30 am
Local community not educated on how to shelter-in-place; also not aware when all-clear called